VII. The Development of the Atomic Theory: (1) Berthollet's Doctrine of Variable Proportions.

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Two of the burning questions in science, between the years 1800 and 1810, were the theory of "mixed gases," and the fixed or the variable composition of chemical substances. On each of these questions Claude Louis Berthollet and John Dalton were leaders of thought on opposite sides, and in each case Dalton's ideas were ultimately triumphant. Yet his rights in these directions have never received full attention, the subjects having been treated in an inadequate manner by the historians of science. The present paper shows in outline how the doctrine of constant proportions developed.

The doctrine that chemical compounds have a constant composition is not a discovery made in the XVIIIth century by a certain man. Lavoisier, Wenzel, and Richter were outstanding workers on the subject, and other workers in the same field, and to much the same general effect, were Cavendish, Bergman, Klaproth, Vauquelin, and Kirwan. Many more might be named, for practically all chemists towards the end of the century seem to have judged the doctrine to be a satisfactory account of the facts of chemistry.

But no doctrine can be regarded as established, or even as rightly understood, until it has been called in question and successfully defended. The challenge puts the defenders on their mettle and compels them to con-

sider, perhaps to realise for the first time, precisely what their position is. Such was the case of the doctrine of constant proportion. It seems to have arisen naturally and been taken for granted, assumed as a matter of course, rather than considered and carefully defined. Suddenly, about the beginning of the XIXth century, it was called in question by Berthollet.

Primarily his teaching was concerned with the problems of chemical affinity. He had ample leisure to meditate on the subject during his stay in Egypt, where he had gone as an honoured member of the famous Napoleonic expedition. The first fruits of that leisure appeared in papers, read in Cairo before the shortlived Institute of Egypt in June of the year 1799, in which he propounded the valuable and original ideas of "mass-action" and chemical equilibrium. Berthollet was thus the founder of *chemical statics*. Resuming the subject on his return to France, he developed his ideas into a system of chemistry, which is explained in various Memoirs[1] and above all in his "Essai de Statique Chimique," (2 vols., 1803).

His teaching aroused interest everywhere, witness the appearance of English and German translations of his works, and the extent to which his ideas permeated the scientific dissertations[2] and books of the period. His main contention that chemical change was very largely a matter of two factors, affinity and mass-action, could hardly be denied. The tables of affinity which in the course of the XVIIIth century had become more and

[1] "Recherches sur les lois de l'Affinité," *Mém. de l'Institut*, vol. 3, pp. 1, 207, 228, 1801 ; vol. 7, 229, 1806.

[2] Memoirs, in which Proust, Thénard, Gay-Lussac, Avogadro, Berzelius, and Dalton take Berthollet's ideas into consideration will be cited as occasion requires. A supplementary list of memoirs not specially referred to in this paper, will be found in an appendix.

more elaborate, were now seen to be obsolete, for they had been drawn up in ignorance of the effects of mass-action. Torbern Bergman, in particular, had prepared more numerous and more elaborate tables than any that had previously appeared, and had also endeavoured to extend the theory of affinity to the reactions of acids, bases, and salts. Berthollet showed that affinity had nothing to do with these reactions, which are governed by mechanical considerations, such as the insolubility and volatility of a substance. Von Meyer, in his "History of Chemistry," advances the opinion that Berthollet's teaching was neglected. "His principles were held to be totally erroneous. . . . . It was thus that Bergman's doctrine, although based upon wrong assumptions, and therefore leading its author to false conclusions, kept for so long a time the upper hand."[3] Ladenburg is much nearer the mark when he remarks that "tables of affinity disappear soon after the appearance of Berthollet's 'Statique Chimique.'"[4] The truth is that Berthollet's ideas supplanted Bergman's with an ease almost unparalleled in the history of science. Karsten remarked in 1803 that not a trace was to be found of our previous ideas on affinity,[5] and as early as 1801, Fischer, who translated Berthollet's "Recherches" into German, declared that the new view of chemical phenomena was so convincing that it was impossible to uphold the old theory.[6]

[3] "Hist. of Chem.," Eng. trans., p. 551, 1906.

[4] "Hist. of Chem.," Eng. trans., p. 41, 1900.

[5] *Allg. J. Chem.*, (Scherer), vol. 10, p. 137.

[6] *Allg. J. Chem.*, (Scherer), vol. 7, pp. 507, 517. It is difficult here to avoid overstating the truth, one way or the other. Of course the disappearance of tables of affinity from the text-books of chemistry, in consequence of Berthollet's teaching, was not absolute. Objections to his teaching were urged by Pfaff in 1811 (see Appendix) and by Davy, "Elements of Chemical Philosophy," pp. 117—124, 1812 (see also Henry, "Elements of Experimental Chemistry," vol. 1, pp. 66—67, 1829). Nevertheless, Berthollet's doctrine of chemical affinity, in its main features, was never seriously challenged.

The time was ripe for a new theory of affinity. That is the explanation of how Berthollet's ideas were taken up so eagerly as was the case. Chemical reactions had been studied in the light of the old theory so thoroughly that numerous anomalies had been discovered, which only the new theory could explain. Even the effect of mass in chemical change had been noted by Bergman. In his "Dissertation on Elective Attractions" (§ 10, 1785) he discusses the reaction, $Ad+c=Ac+d$, where Ac is precipitated. "It now remains to be examined, whether the whole of d can be dislodged by a sufficient quantity of c from its former union. It should be carefully noted in general, that there is occasion for twice, thrice, nay sometimes six times the quantity of the decomponent c, than is necessary for saturating A when uncombined." Bergman noted the effect, but could not explain the principle, of mass-action. That principle, leading straight as it does to the doctrine of chemical equilibrium, was quite foreign to the theory of chemical affinity to which he always adhered.

It seemed to be a necessary consequence of Berthollet's principles that chemical combination takes place in indefinite proportion. He had obliterated the distinction between chemical and physical forces, and regarded solution as produced by affinity between solvent and solute. Hence solutions were compounds.[7] In the next place, indefinite proportion seemed to be an obvious corollary of his "mass-action" theorem. In any chemical system the state of equilibrium depends on the quantity present of each of the re-agents involved. Hence the larger the amount of a given constituent that might be present, so much the more of this should enter into the composition

[7] "Essai de Statique chimique," §§ 36, 39.

of the product. So he reasoned. For instance, if hydrochloric acid is added to a solution of copper sulphate in water, the copper is divided between the two acids. It was natural to think that all the hydrochloric acid was combined with its share of the copper, and all the sulphuric acid with its share.[8]

Berthollet's attitude is easily misunderstood. He did not so much contradict as transcend the XVIIIth century view. He did not assert that cases of constant composition were non-existent. He admitted, for instance, those of water and ammonia and the oxides of mercury, and was inclined to think that gases combine in constant proportion.[9] But he thought these instances arose from exceptional circumstances, which he was perfectly prepared to discuss. His standpoint was that constant composition was the exception, and variable composition the rule.[10]

On this matter his great opponent was Joseph Louis Proust. The battle waged chiefly round the oxides of the metals. In the case of a metal which forms more than one oxide, Berthollet held that the oxide at minimum can gradually increase its oxygen without sudden change, till the oxide at maximum is reached. Proust, on his part, while not denying that a metal might yield more than two oxides, directed all his efforts to the study of the two extreme oxides,[11] and showed that material of intermediate composition usually consisted of a mere mixture of these two,[12] and

[8] *Op. cit.*, § 52. But the instance given above is not Berthollet's.

[9] *Op. cit.*, §§ 206, 207.

[10] *Jour. de Phys.*, vol. 60, p. 347, 1805.

[11] *Op. cit.*, vol 63, pp. 438—440, 1806.

[12] *Op. cit.*, vol. 55, p. 331, 1802.

he maintained his point with great conviction and persistence.[13]

The historians of chemistry have not been well inspired in their estimates of the meaning and the result of this controversy.[14] They convey the impression that Berthollet was a person who had "preposterous notions" about the chemical composition of substances and was "deservedly annihilated"[15] by Proust. Ladenburg[16] says the controversy was settled by the year 1809, Kopp[17] and Clarke[18] in 1808,

[13] Proust's principal memoirs on the subject are:

(1) Recherches sur le cuivre. *Ann. de Chim.*, vol. 32, pp. 26—54, 1799.

(2) Sur quelques sulfures métalliques. *Jour. de Phys.*, vol. 53, pp. 89—97, 1801.

(3) Mémoir pour servir à l'histoire de l'antimoine. *Op. cit.*, vol. 55, pp. 325—344, 1802.

(4) Sur les sulfures métalliques. *Op. cit.*, vol. 59, pp. 260—265, 1804.

(5) Sur les sulfures alcalins. *Op. cit.*, vol. 59, pp. 265—273, 1804.

(6) Sur les oxidations métalliques. *Op. cit.*, vol. 59, pp. 321—343, 1804.

(7) Sur les muriates de cuivre verd et blanc. *Op. cit.*, vol. 59, pp. 350—354, 1804.

(8) Faits pour l'histoire du cobalt. *Op. cit.*, vol. 63, pp. 421—442, 1806.

In all probability Berthollet's ideas on affinity and chemical composition were first made known through his lectures at the *École Normale* and the *École Polytechnique*. In 1799, before the "Recherches sur les lois de l'affinité" had appeared, Thénard published a paper in support of Berthollet, and Proust one against him. For Berthollet in reply to Proust, see the "Recherches" and the "Statique Chimique," and also "Observations relatives à differens mémoires de Proust," *Jour. de Phys.*, vol. 60, pp. 284—290, 347—351, 1805; vol. 61, pp. 352—362, 1805.

[14] From these strictures I must except P. J. Hartog, who has given in brief a perfectly just statement of the question at issue, see *Nature*, vol. 50, p. 149, 1894, and also *Brit. Ass. Rep.*, p. 618, 1894.

[15] See Huxley on Descartes and Newton.

[16] "Hist. of Chem.," Eng. trans., p. 45, 1900.

[17] "Geschichte der Chem.," vol. 2, p. 369, 1844.

[18] *Manchester Memoirs*, vol. 47, No. 11, p. 9, 1903.

and E. von Meyer[19] in 1807. A. Wurtz, putting the date even earlier, says "the truth of the fixity of chemical proportion was definitely established in the year 1806."[20]

These writers do not adduce any evidence in support of their statements. They seem to consider their case so probable that proof is unnecessary. On the contrary their case is not even probable. It depends on a fatal underestimate of the influence of Berthollet. He occupied a commanding position in the world of science, so that his ideas could not fail to receive consideration in full. Not only were his main ideas of the highest intrinsic value but his teaching on the very subject of constant proportion, in the light of the knowledge which was then available, was extremely plausible. There are two reasons for this. First, chemists in the XVIIIth century had concentrated their attention on the outstanding compound of each pair of elements, and on this insufficient basis the doctrine of constant composition had been founded. Berthollet raised a new problem by studying the relation between the different compounds of the same elements. It has already been suggested that his teaching did not so much contradict Lavoisier's and Wenzel's and Richter's as go beyond it. While holding in general that affinity tends to unite substances in all proportions, he pointed out that this tendency could be limited by physical factors such as cohesion and insolubility and elasticity, in which case the compounds would be produced on which the supposition of fixed proportion had been based.

In the second place the wretched state of chemical analysis only too easily afforded data in support of variable proportion. Berthollet's theory suited the existence of discordant analyses of the same substance by

[19] "Hist. of Chem.," Eng. trans., p. 194, 1906.

[20] "The Atomic Theory," Eng. trans., p. 9, 1880.

different workers and even by the same worker. He was able to maintain his teaching by quoting able chemists such as Vauquelin and Klaproth, whose results *a priori* were as probable as Proust's.[21]

Proust had to maintain his own analyses in the face of Berthollet's teaching and of the analyses of other chemists. It is quite a mistake to suppose that his results were specially accurate. E. von Meyer surmises that if he had only "calculated the result of his experiments on the composition of binary compounds otherwise than he did, he would have discovered the law of multiple proportions."[22] As a matter of fact he frequently expressed his results in a way that must have revealed the law in question, supposing that he had known what to look for, and that his data were approximately correct. For the composition of black oxide of copper he gives copper 100 and oxygen 25, and this is correct, and for the composition of the red oxide copper 100, and oxygen 17—18 instead of 12·5.[23] These figures prove that for the determination of the composition of chemical substances it is not sufficient to have good intentions and a strong conviction that substances are formed in invariable proportions.

In truth the odds against Proust were heavy. He had no principle of the same calibre as the doctrines of mass-action and chemical equilibrium with which to encounter Berthollet. He had to trust to the purely empirical method, and there is no reason to think that it was by means of this method that the doctrine of constant proportion was ultimately established.

[21] *Jour. de Phys.*, vol. 60, p. 349, 1805.

[22] *Op. cit.*, pp. 195—196; see also Arrhenius to the same effect, "Theories of Chemistry," Eng. Trans., p. 16, 1907.

[23] *Journ. de Phys.*, vol. 65, p. 80, 1807.

E. von Meyer says that "none of the other leading chemists of the day raised any objections."[24] This puts the matter too strongly, for Thénard, who had previously been on Berthollet's side, showed signs of veering round in 1805. "I am quite persuaded that the number of oxides of the metals is much greater than the majority of chemists allow, . . . but I declare that I am not yet convinced that there are as many oxides as there are possible degrees of oxidation; and if theory allows of them, experience seems to reject them."[25] In this paper he maintains that there are not two oxides of iron (as Proust said) but three.[26] Proust must have had some adherents, but I do not know of any, unless Thomas Thomson be one,[27] who gave him open support. Thénard does not mention him. There is extremely little sign that he was considered to have made out his case. Further, there is every reason to think that the change of opinion, when it came, was due to quite another influence than Proust. What was effective was the working hypothesis which the atomic theory supplied.

The influence of Dalton began to permeate chemistry about the year 1808. For some years he had been making endeavours, not very successful ones, to arouse interest in his theory of chemical combination. In particular, Humphrey Davy,[28] with all his powers of imagination, had failed to see anything in it. A much less

[24] "Hist. of Chem.," Eng. trans., p. 194, 1906.

[25] *Ann. de Chim.*, vol. 56, p. 62, 1805.

[26] *Op. cit.*, pp. 66, 77.

[27] See *Nicholson's Journ.*, vol. 8, pp. 280—281, 1804.

[28] Davy must surely have heard of the atomic theory when Dalton was lecturing at the Royal Institution of London in 1803—1804 (see Henry's "Life of Dalton," pp. 47—50, and Dalton's "New System of Chemical Philosophy," p. v., 1808). He certainly discussed it with Thomas Thomson in 1807 and poured ridicule on it then. (See Thomson's "History of Chemistry," vol. 2, p. 293.)

brilliant man than Davy, Thomas Thomson by name, happening to get an account of the theory from Dalton himself in the year 1804, was wise enough to see its immense importance, and in the year 1807 gave an admirable sketch of it in the 3rd edition of his "System of Chemistry." Then in 1808 Dalton gave his own version of it in the first instalment of his "New System of Chemical Philosophy." Confirmation of the theory had already appeared. At the beginning of the year Thomson had published work on the oxalates of strontium, and William Hyde Wollaston on the carbonates and oxalates of potassium, which they each regarded as exemplifying and justifying Dalton's teaching. This work was of great importance at the moment. As Wollaston remarked afterwards, "Chemists were by no means duly impressed with the importance of this observation of Dalton, until they were in possession of other facts observed by Mr. Thomson and myself."[29] The historians of chemistry have failed to perceive the full significance of this work. It refuted Berthollet in a specially telling way, for, in illustrating his doctrine, he had made much use of acid salts of the kind that Thomson and Wollaston examined. He had found them to be of variable composition,[30] and now, in the light of Dalton's theory, they were found to be perfectly definite substances.

[29] *Phil. Trans.*, p. 6, 1814.

[30] "Essai de Statique Chimique," §§ 201—203; *Mém. de l'Institut*, vol. 7, pp. 230—252, 297, 1806. Not only so, but Torbern Bergman ("Dissertation on Elective Attractions," § 9) and J. B. Richter (see report by Karsten of a conversation with Richter, *Allg. J. Chemie*, (Scherer), 10, 138—143, 1803) thought that in many cases salts could be formed with a decided superfluity of either ingredient. Further, it has been shown recently (Joh. D'Ans, *Zeitsch. anorg. Chem.*, 63, 225—229, 1909) that there are four acid sulphates of potassium; hence Berthollet might well think that these salts justified his belief in variable proportion: (see his Introduction to Riffault's translation of Thomson's "System of Chemistry," vol. 1, p. 24.)

That Berthollet felt the weight of this refutation of his teaching is shown by the fact that he thought it necessary to repeat Wollaston's experiments.[31]

Further, Gay-Lussac's Memoir on the combining volumes of gases, published in 1809, afforded numerous examples amongst gases of combination in fixed proportion. Berthollet, however, had declared that this was likely to occur amongst gases, a fact which greatly discounted the possible effect on chemists of Gay-Lussac's discovery—of tending to lessen their confidence in Berthollet's doctrine of variable proportion. Besides, at that stage of chemistry, Gay-Lussac was himself reluctant to abandon this doctrine, and still held that, in general, mass-action must produce compounds in all proportions. He maintains the "great chemical law, that whenever two substances are in presence of one another, they act in their sphere of activity according to their masses, and give rise in general to compounds with very variable proportions, unless these proportions are determined by special circumstances."[32]

Indeed, Dalton's doctrine of combination in definite and multiple proportions was victorious only in process of time and in consequence of the efforts of J. J. Berzelius. Yet it is worth noticing how much less complete Proust's answer to Berthollet was, than the answer tacitly conveyed by Dalton's doctrine. Berthollet held that affinity tends to combine elements in all proportions, and that the composition of the oxides of a metal at maximum and minimum depended on accidental factors, physical conditions opposed to affinity, such as cohesion and elasticity. Dalton showed that a beautifully simple relation exists between the composition of one oxide and another, so

[31] *Mém. d'Arceuil*, vol. 2, p. 470, 1809.

[32] *Op. cit.*, pp. 232—233.

that the composition is not in the least a matter of chance. Proust had no conception of the law which regulates multiple proportions. Again, Berthollet believed that one oxide could change into the other by continuous variation in composition, while Dalton's theory not only allowed for the existence of definite intermediate oxides, but could even predict their composition with a considerable degree of certainty.

The view taken here, that Berthollet's teaching on the subject of chemical composition easily survived Proust's criticism, and received a serious check from Dalton, can be amply illustrated from the literature of the time. William Henry treats the subject of chemical proportion in that sense. "In opposition to the theory that chemical affinity has a strong tendency to unite bodies in unlimited proportions, an hypothesis has lately been proposed by Mr. Dalton, which appears more consonant to the general simplicity of nature."[33] John Murray pits the two doctrines against one another, and actually, as late as the year 1809, expresses a strong preference for Berthollet's.[34] Indeed, Berthollet felt the challenge to himself implied in Dalton's Atomic Theory, and showed this by criticising it in the Introduction which he contributed to the French translation of Thomson's "System of Chemistry,"[35] in which, it will be remembered, the theory is sketched.

If anyone, inclining to hold to the view of von Meyer and Wurtz that Proust was successful against Berthollet, should doubt whether the prestige of the latter was so great as has been indicated in this paper, he might do well to consider the chemical literature of the time. In

[33] "Elements of Experimental Chemistry," 6th ed., vol. 1, p. 81, 1810.

[34] "System of Chemistry," 2nd ed., vol. 1, p. 627.

[35] Riffault's translation, vol. 1. pp. 21—27, 1809.

addition to Gay-Lussac and Murray, who, as already explained, adhered in the year 1809 to the doctrine of combination in variable proportion, Friedrich Stromeyer[36] in 1808, and Amadeo Avogadro[37] in 1811, showed themselves under the sway and influence of Berthollet. What is more, even after Dalton's doctrine of definite proportion had become the foundation of chemistry, Berthollet's main ideas were still held by chemists in the greatest respect. The very opposite of this might be inferred from E. von Meyer's statement that "his principles were held to be totally erroneous . . . . . the revival of his principles was reserved for quite modern times,"[38] and Sir William Ramsay's conjectural remark that the "Essai de Statique Chimique" was soon forgotten."[39]

Berzelius's "Essai sur la Théorie des Proportions Chimiques," published in 1819, contains an exposition of mass-action and chemical equilibrium,[40] and is dedicated "a l'auteur de 'L'essai de statique chimique.'" Perhaps the most interesting testimony of this kind is borne by J. B. Dumas, who in his lectures on chemical philosophy, delivered in the year 1836, expressed the highest admiration for the "Statique Chimique." "It engrossed my whole time for three or four years; from the age of 17 to 21 I read it, re-read it, and pondered it. . . . . I read it pen in hand, making extracts and reflections and comments; these efforts have been of the highest value to me. As a student of chemistry I formed myself on Berthollet . . . . and whatever right I have to raise

[36] "Grundriss der Theoretischen Chemie," pp. 66, 80.

[37] *Jour. de Phys.*, vol. 73, p. 76.

[38] *Op. cit.*, p. 551.

[39] "Introduction to the Study of Physical Chemistry," p. 43, 1904.

[40] *Op. cit.*, pp 7—11, 106—109.

my voice in this hall . . . . I owe it to the study I made of Berthollet's 'Statics.'" [41]

Finally, on the establishment of these two doctrines, which seemed to be incompatible with one another—Dalton's of invariable proportions and Berthollet's of mass-action—there remained the problem of reconciling the one with the other. That the necessity of doing this was present in the minds of the leaders of chemistry is proved by Berzelius's "Essay on the cause of Chemical Proportions," etc., which begins with a section "on the relation between Berthollet's theory of affinities and the laws of chemical proportions." He remarks that "some chemists have affirmed that the existence of chemical proportions is contrary to the principles of the theory of affinities with which the illustrious Berthollet has enriched chemistry," and proceeds to show that this is really not the case. He takes the case of solution in water of copper sulphate to which hydrochloric acid is added; ". . . . the part of the acid really combined with the oxide is neutralised according to the laws of chemical proportions. . . . . This single example is sufficient to show that the principles of Berthollet's theory are not inconsistent with the laws of chemical proportions." [42]

Dalton, in his comments on this Essay, expresses his full concurrence with the verdict. "The first division of Dr. Berzelius's essay contains an admirable exposition of those facts which Berthollet brought forward in so conspicuous a point of view in his chemical theory, and which his zealous followers have magnified in a still greater degree. A better explanation could, I think, be scarcely given in fewer words." [43]

[41] "Leçons sur la Philosophie Chimique," pp. 379—380

[42] *Ann. of Phil.*, vol. 2, p. 443, 1813.

[43] *Ann. of Phil.*, vol. 3, p. 174, 1814.

APPENDIX.

List of Memoirs, in addition to those mentioned in the paper, which show Berthollet's influence.

1799.

L. J. Thénard, "Les différents états de l'oxide de l'antimoine et ses combinaisons avec l'hydrogène sulfuré," *Ann. de Chim.*, vol. 32, pp. 257-269.

1800.

(A note drawing attention to Berthollet's work on the causes of error in tables of affinity.) *Allg. J. Chemie* (Scherer), vol. 4, pp. 669-670.

1801.

"Ueber den Einfluss einiger unbeachteten Umstände bei der Wirkung der Wahlverwandschaften," *Chem. Ann.* (Crell), vol. 1, pp. 111-114.

1802.

L. J. Thénard, "Sur les différentes combinaisons du cobalt avec l'oxygène, etc," *Ann. de Chim.*, vol. 42, pp. 210-219.

1803.

A. B. Berthollet, "Observations sur les précipités des dissolutions métalliques," in "Essai de Statique Chimique," note 22.

E. G. Fischer, "Vermischte Bemerkungen über die brennbaren Grundstoffe, mit Rücksicht auf Berthollets Theorie der Verwandschaft," *Allg. J. Chem.* (Scherer), vol. 10, pp. 171-184.

L. W. Gilbert, *Ann. der Phys.*, vol. 13, pp. 158-159.

C. J. B. Karsten, "Revision der Chemischen Affinitätslehre mit beständiger Rücksicht auf Berthollets neuer Theorie," Leipzig, pp. 278.

L. Schnaubert, "Untersuchung der Verwandschaft der Metalloxyde zu den Säuren. Nach einer Prüfung der neuen Bertholletschen Theorie," Erfurt (for Berthollet's comments on this, see *Ann. de Chim.*, vol. 49, pp. 5-20, 1804).

1804.

Gay-Lussac, "Sur les précipitations mutuelles des oxides métalliques," *Ann. de Chim.*, vol. 49, pp. 21-35.

1805.

J.-M. HAUSMANN, "Sur l'oxidation," *Ann. de Chim.*, vol. 56, pp. 5-14.

1807.

C. F. BUCHOLZ, "Die Verhältnissmengen der Bestandtheile im salzsauren Silber, und den salzsauren Neutralsalzen," *J. für Chem.* (Gehlen), vol. 3, pp. 328-335.

A. F. GEHLEN [notes accompanying his translation into German of Berthollet's "Troisieme Suite de Recherches sur les lois de l'affinité."] *J. für Chem.* (Gehlen), vol. 3, pp. 248-322.

H. F. LINK, "Ueber Berthollet's Theorie der Chemischen Verwandschaft," *J. für Chem.* (Gehlen), vol. 3, pp. 232-247.

ROSE, "Die Verhältnissmengen der Bestandtheile des Schwefelsauren Baryts," *J. für Chem.* (Gehlen), vol. 3, pp. 322-328.

1808.

H. F. LINK, "Einige Bemerkungen über Anziehung und Verwandschaft," *Ann. der Phys.*, vol. 30, pp. 12-22.

1811.

L. W. GILBERT, "Historische-Critische Untersuchung über die festen Mischungs-Verhältnisse in der Chemischen Verbindung, etc.," *Ann. der Phys.*, vol. 39, pp. 361-428.

C. H. PFAFF, "Expériences et observations relatives au nouveau principe d'action de l'affinité établie par M. Berthollet," *Ann. de Chim.*, vol. 77, pp. 259-288 (for Berthollet's comments on this, see *op. cit.*, 288-296).

G. K. L. SIGWART, "Ueber Berthollet's Chemische Masse," *J. für Chem.* (Schweigger), vol. 1, pp. 352-357.

1812.

P. L. DULONG, "Recherches sur la décomposition mutuelle des sels solubles et des sels insolubles," *Ann. de Chim.*, vol. 82, pp. 273-308.

1815.

H. F. LINK, "Ueber die Chemische Wirkung beim Zusammenreiben der Körper," *J. für Chem.* (Schweigger), vol. 14, pp. 193-199.

Manchester Memoirs, Vol. lv. (1910), *No.* 3.

III. The Development of the Atomic Theory: (2) The various Accounts of the Origin of Dalton's Theory.

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The origin of Dalton's theory remains one of the outstanding problems in the history of chemistry. Yet the amount of material at hand for the study of the subject is considerable. Dalton's note-books, discovered within the last twenty years in the rooms of the Manchester Literary and Philosophical Society, contain material of the highest value for the purpose. Also, there are on record important accounts of the genesis of the theory by three different persons. One is given by William Charles Henry, another by Thomas Thomson, and another by Dalton himself. Although there are yet other accounts in existence, these three are the only ones that need be considered in detail here.

One of the principal results of this paper is to show that these various narratives came, originally, from Dalton himself. In the nature of the case, this is what was to be expected. At the same time the discrepancies between these accounts have to be explained. In the course of the paper it will become more and more evident that the person responsible for them is Dalton.

December 17th, 1910.

1. *The Influence of J. B. Richter.*

William Charles Henry held a conversation with Dalton on the subject of the origin of the theory, in which special importance was given to the influence of J. B. Richter. "The speculations which gave birth to the atomic theory were first suggested to Mr. Dalton by the experiments of Richter on the neutral salts . . . a table was formed exhibiting the proportions of the acids and the alkaline bases constituting neutral salts. It immediately struck Mr. Dalton that if these saline compounds were constituted of an atom of acid and one of alkali, the tabular numbers would express the relative weights of the ultimate atoms. These views were confirmed and extended by a new discovery of Proust,"[1] &c.

This narrative received strong support from William Henry (the father of W. C. Henry), who held more than one conversation with Dalton on the subject. The following is part of a minute, dated February 13, 1830, of one of these conversations :—"Confirmed the account he before gave me of the origin of his speculations leading to the doctrine of simple multiples, and of the influence of Richter's table in exciting these views."[2]

The Henrys, father and son, are entitled to the fullest credence in this matter. Their acquaintance with Dalton was more intimate than that of any other man of science, Peter Clare excepted. W. C. Henry was in turn the pupil, the friend and the biographer of Dalton. In the preface to the Biography, he mentions with just pride Dalton's "almost lifelong friendship with my father, never shadowed by even a passing cloud"; and he refers also to "his early favourable notice of and unceasing benevolent regard towards myself, thoughtfully mani-

[1] W. C. Henry, "Memoirs of Dalton," p. 84.

[2] *Ibid.*, p. 63.

fested in his last bequest to me of what he had most prized in life." This was the bequest of all his chemical and philosophical instruments and apparatus. Other proofs of this friendship can easily be found. There is the dedication of Dalton's "New System of Chemical Philosophy" (vol. i., Part 2) to William Henry (along with Humphrey Davy), and of Henry's "Elements of Experimental Chemistry" (6th Ed., 1810) to Dalton. Again, Dalton took an opportunity in 1827 of acknowledging his friendship with William Henry. "It affords me great pleasure to acknowledge the continued and friendly intercourse with Dr. Henry, whose discussions on scientific subjects are always instructive, and whose stores are always open when the promotion of science is the object."[3]

There is no room for doubt that the reports of these conversations with Dalton are perfectly authentic. W. C. Henry states that he noted down Dalton's expressions "immediately after each lesson," and the passage which has been quoted, regarding the influence of Richter, is copied, he says, "verbatim from my own journal when his pupil."[4] Nevertheless, Henry knew there was something wrong. The date of his conversation with Dalton was February 5, 1824, and he says, "on reviewing in conversation, after the lapse of twenty years, the labours of the past, Dalton himself may have failed in recalling the antecedents of his great discovery in the exact order of sequence"[5]

Again, the Richter story is strongly challenged by Thomas Thomson. "When I visited him in 1804 at Manchester both Mr. Dalton and myself were ignorant of

[3] "New System of Chemical Philosophy," vol. 2, p. 8, 1827.

[4] *Ibid.*, p. 84.

[5] *Ibid.*, p. 86.

what had been done by Richter on the same subject." Again, "Nobody knows better than myself that Dalton was ignorant of what Richter had done about ten years before him."[6] This shows conclusively that Dalton said nothing about Richter to Thomson.

Now that we have access, thanks to Roscoe and Harden's "New View of the Origin of Dalton's Atomic Theory," to the valuable material contained in Dalton's notebooks, we can carry the critical process further than Henry and Thomson did. The notebooks show, as Roscoe and Harden point out, that Dalton had been busily engaged during the year 1803 on the atomic theory, and that he was investigating the non-metallic elements then, and not Richter's acids and bases at all.

Dalton's knowledge of Richter can hardly have been due to anyone but Berthollet. Richter's work had been completely ignored till E. G. Fischer gave a resumé of it, and thus made it known throughout Germany. Berthollet, by quoting this resumé at the end of the "Essai de Chimie Statique," made Richter known throughout Europe. In the "Essai" Berthollet opposes Dalton's theory of "mixed gases," but Dalton made no reply till 1808 in the "New System of Chemical Philosophy." This helps to date his knowledge of Richter. If Dalton was slow to read new books, he was prompt in replying to criticisms of his theory. He kept up the defence of it in a series of papers which came to an end about October, 1805, without any mention of Berthollet's objections having been made. It was presumably subsequent to this date that Dalton read the "Essai," and learnt of Richter's work. In the note-books the date of the earliest reference to Richter is April 19th, 1807.[7] There is really no room for doubt that

[6] *Proc. Phil. Soc. Glasgow*, vol. 2, pp. 86, 88, 1845-6.

[7] Roscoe and Harden, "New View of the Origin of Dalton's Atomic Theory," p. 79; see also pp. 7-10, 46, 91-94.

Dalton's declarations in 1824 and 1830 to one and the same effect regarding the influence of Richter must be set aside.[8]

2. *The Composition of Marsh-gas and Olefiant Gas.*

Thomas Thomson says that the theory first occurred to Dalton during his investigation of marsh-gas and olefiant gas. The discovery of the composition of these gases led to the discovery of the law of multiple proportion, and the theory was then devised in order to explain the law. His exact words are :—

"Mr. Dalton informed me that the atomic theory first occurred to him during his investigations of olefiant gas and carburetted hydrogen gas, at that time imperfectly understood, and the constitution of which was first fully developed by Mr. Dalton himself. It was obvious from the experiments which he made upon them that the constituents of both were carbon and hydrogen, and nothing else. He found, further, that if we reckon the carbon in each the same, then carburetted hydrogen contains exactly twice as much hydrogen as olefiant gas does. This determined him to state the ratios of these constituents in numbers, and to consider the olefiant gas a compound of one atom of carbon and one atom of hydrogen ; and carburetted hydrogen of one atom of carbon and two atoms of hydrogen. The idea thus conceived was applied to carbonic oxide, water, ammonia, &c., and numbers were given representing the atomic weights of oxygen, azote, &c., deduced from the best analytical experiments which chemistry then possessed."[9]

This narrative has passed muster for many years, and is better known than any other. It was accepted with

[8] Roscoe and Harden, *loc. cit.*

[9] Thomas Thomson, "History of Chemistry," vol. 2, p. 291.

reservations by W. C. Henry[10] and Angus Smith[11], and by Roscoe and Schorlemmer[12] without objection. Owing to the large circulation of Roscoe and Schorlemmer's book, this version of the origin has decided the opinion of the generality of chemists. There is, nevertheless, the best reason for thinking that marsh-gas and olefiant gas did not have the effect which it assigns to them of leading to the theory.

Indeed, in 1811, Dalton connected the theory in its early days with the oxides of nitrogen:—"I remember the strong impression which at a very early period of these inquiries was made by observing the proportion of oxygen to azote, as 1, 2, and 3, in nitrous oxide, nitrous gas, and nitric acid, according to the experiments of Davy."[13] Thomson must have seen the necessity of abandoning the marsh-gas and olefiant gas story, for he said in 1850:—"Dalton founded his theory on the analysis of two gases, namely, protoxide and deutoxide of azote."[14]

Dalton's work on marsh-gas appears in the note-book under date 6th August, 1804. Roscoe and Harden[15] point out that he had been busily engaged on the theory the year before. He had even arrived at the fundamental ideas of his system, and had constructed a table of atomic weights by September 6th, 1803.

Obviously, Thomson's account of the origin of the theory is untrustworthy, inasmuch as marsh-gas and olefiant gas had no part in the matter. The question arises, who is responsible for the error, Thomson or Dalton? Before answering this question it is necessary

[10] "Memoirs of Dalton," p. 80.

[11] "Memoir of Dalton," p. 231.

[12] "Treatise on Chemistry, Non-metallic Elements," p. 36, 1877.

[13] *Nicholson's Journ.*, vol. 29, p. 143, 1811.

[14] *Proc. Phil. Soc. Glasgow*, vol. 3, p. 140, 1850.

[15] *Op. cit.*, p. 28.

to consider carefully the relations between the two men and the circumstances under which Thomson's narrative arose.

Thomson, unlike the Henrys, was not a personal friend of Dalton. He had made an adverse criticism of a certain theory of which Dalton was the author, and the author had made a stiff rejoinder.[16] He thereupon paid a visit to Manchester with the object of arriving at a full understanding of the matter in question. The date of the interview was August 27th, 1804, and it was then, by a fortunate accident, that Thomson learnt of the chemical atomic theory of Dalton.

Again, it is certain that Thomson and Dalton were not subsequently in frequent communication with one another on the subject. The sketch of the theory, which Thomson published in 1807, was accompanied by the note :—" In justice to Mr. Dalton, I must warn the reader not to decide upon the notions of that philosopher from the sketch which I have given, derived from a few minutes conversation, and from a short written memorandum. The mistakes, if any occur, are to be laid to my account, and not to his ; as it is extremely probable that I may have misconceived his meaning in some points."[17]

Nevertheless, this footnote errs on the side of caution. Thomson's sketch of the theory, giving the first account of it ever printed, was based on notes of what Dalton told him, made during the interview, and only one phrase in it is open to objection. He showed both zeal and care in the matter, for it strongly interested him.

In the "History of Chemistry," published in 1831, Thomson says :—" I wrote down at the time the opinions which he offered, and the following account is taken

[16] See *Nicholson's Journ.*, vol. 8, p. 145, 1804 ; and *Annals of Philosophy*, vol. 4, p. 65, 1814.

[17] Thomas Thomson, "System of Chemistry," 3rd Ed., vol. 3, p. 425, 1807.

literally from my journal of that date."[18] Then comes an account of the atomic theory, and on that there follows the passage already quoted, connecting marsh-gas and olefiant gas with the genesis of the theory. Here the question arises, is all this taken from the journal, both the sketch of the theory and of how the theory arose? Only an examination of the journal can settle this point, but I have not succeeded in ascertaining where it is kept, if, indeed, it is still in existence.

It must be admitted also that Thomson seems to become more and more positive regarding the genesis of the theory as time goes on. The account which I have been considering was published in 1831. Six years earlier he had advanced the same account in a more hesitating way:—"Unless my recollection fails me, Mr. Dalton's theory was originally deduced from his experiments on olefiant gas and carburetted hydrogen."[19] Yet there is no intrinsic improbability that Thomson's recollection is correct. One cannot doubt that during the interview Dalton was much less interested in the question of the origin than in the theory itself. If Thomson inquired about the origin, Dalton may have made the inquiry an opportunity of expounding the theory in terms of its latest triumph, namely, the composition of marsh-gas and olefiant gas.

3. *The Amended Theory of "Mixed Gases."*

There remains for consideration the account which Dalton gave in a lecture (the 17th of a series) at the Royal Institution of London, on the 27th January, 1810. The

[18] Thomas Thomson, "History of Chemistry," vol. 2, p. 287.

[19] Thomas Thomson, "An Attempt to Establish the First Principles of Chemistry by Experiment," vol. 1, p. 11, 1825.

notes for it still exist in his own handwriting, and were found, along with his notebooks, in the rooms of the Manchester Literary and Philosophical Society. He begins by discussing his physical atomic theory, which aimed at explaining the diffusion of gases. He entertained two diffusion hypotheses, the first of which originated in 1801, while an amended hypothesis, he says, was formed in the year 1805. He had not at first "contemplated the effect of *difference of size* in the particles of elastic fluids." On consideration, he "found that the *sizes must* be different," and subsequently arrived at a different explanation of the mechanism of diffusion from the one he at first suggested.

He then introduces the subject of the chemical atomic theory:—"The different *sizes* of the particles of elastic fluids under like circumstances of temperature and pressure being once established, it became an object to determine the relative *sizes* and *weights*, together with the relative *number* of atoms in a given volume. This led the way to the combination of gases . . . other bodies besides elastic fluids, namely, liquids and solids, were subject to investigation, in consequence of their combining with elastic fluids. Thus a train of investigation was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination one with another."[20]

This narrative is certainly right on a vital matter. It recognises that Dalton had been using a physical atomic theory, from which he passed to a chemical one. Here there is a common ground of objection to the communications made by Dalton to Thomson and Henry respectively. They both ignore the connection, which certainly existed, between the physical and chemical theories. Thomson did not feel this defect, but Henry

[20] Roscoe and Harden, *Op. cit.*, pp. 16—17.

did. While not denying the influence of Richter, he sums up the evidence on the subject as "unequivocally demonstrating the genesis of the atomic theory as a general physical conception from the study of matter in the *aëriform* condition, and its first practical application in chemistry to *gaseous* bodies, and emphatically to such as combine *in multiple proportions.*"[21] There is no question here of extraordinary insight and discernment on Henry's part. He has simply considered the use Dalton had made of the physical atomic theory previous to forming a chemical one.

Roscoe and Harden have not paid sufficient attention to this. They say "It is . . . . well known that Dalton was an ardent adherent of the Newtonian doctrine of the atomic constitution of matter . . . . It now appears that it was from this physical standpoint that Dalton approached the atomic theory, and that he arrived at the idea that the atoms of different substances have different weights from purely physical considerations."[22] There is really not sufficient justification for Roscoe and Harden's suggestion that they had found in Dalton's narrative a *new* view of the genesis of his atomic theory. The view is to be found in Henry, and might be formed by any person who should read with understanding Dalton's "Essay on the Constitution of Mixed Gases," which was written in 1801, and published in 1802.

There is, however, a fundamental objection to Dalton's narrative. It has a deceptive appearance of being historical. Dalton was a pioneer of science, and a pioneer is a man who must make many mistakes and experience many failures. He has taken a number of different scientific movements and marshalled them, so that they are invested

[21] W. C. Henry, *Op. cit.*, p. 84.

[22] Roscoe and Harden, *Op. cit.*, p. viii.

with the appearance of a deliberate, strategical, irresistible advance. On examination his narrative, in spite of its grand air, is found to throw much less light than it promises on the line of thought and train of investigation which he pursued. It is excessively abstract in tone, and avoids going into details and particulars and instances. It does not tell us what we want to know most, how and when Dalton arrived at the law of multiple proportions, and the part played by the law in the construction of the theory. Information on these matters is what is wanted, and anything else is beside the point.

Yet there is one novel element in Dalton's account. This is the suggestion that the formation of the chemical atomic theory took place subsequently to the amendment of the diffusion theory. But, as the notebooks show, the chemical theory was formed in 1803. Hence, Roscoe and Harden conclude that 1805, the date which Dalton assigns to his amended diffusion theory, should be 1803.[23] Reasons will be given later, in a paper on Dalton's physical atomic theory, for thinking that the narrative is doubtful on the only point on which it presents any novelty.

Conclusion.

There are in existence yet other accounts of this matter. One is given by Dalton's pupil, Joseph A. Ransome,[24] and another by Dalton himself. This was in the lecture which he delivered to the members of the Mechanics' Institute in Manchester on October 19th, 1835.[25] The main feature, which *all* the accounts have in

[23] *Op. cit.*, p. 25.

[24] W. C. Henry, *Op. cit.*, pp. 220-222.

[25] *Manchester Times*, October 25, 1835.

common, is that each originated with Dalton. Thomson's narrative and Henry's and Ransome's were based on conversations with him, and there is no ground for impugning their accuracy any more than his good faith. The natural explanation of the existence of so many and various accounts is that Dalton was simply deficient in historical instinct. He did not perceive the difference between describing the genesis of his theory and expounding the theory itself.

A man who makes history, as Dalton did, need not be a good historian. The account of the origin of the chemical theory in his own handwriting is no more satisfactory than the others which came from him at second-hand. Apparently, Dalton never had in his mind a precise view of how the theory developed, and when invited to give one he produced, on the spur of the moment, an account to which he did, or did not, adhere on the next occasion.

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IV. The Development of the Atomic Theory: (3) Newton's Theory, and its Influence in the Eighteenth Century.

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One of the great obstacles to a right understanding of the history of science, is the tendency of writers to let their attention be absorbed by a single individual, who thus engrosses the credit for important ideas and discoveries, to the neglect of deserving predecessors. This method, besides being unjust, gives a distorted view of the progress of science. For instance, Nernst, apropos of Dalton, remarks that the atomic hypothesis "by one effort of modern science, arose like a phœnix from the ashes of the old Greek philosophy"[1] This sweeping statement ignores atomic speculation between the time of Lucretius and the nineteenth century. As if the atomic theory of Newton, for instance, were perfectly negligible!

This paper is written in the belief that the atomic theory has gone through a process of development from the time of Leucippus up to the present. The main conclusions are that Newton made a contribution to the said process, that he did so under the influence of Descartes, and that he was, in turn, himself an influence in the eighteenth century. It is therefore divided into two parts: (1) The atomic theory of Newton, and (2) Newton's influence in the eighteenth century.

[1] Nernst, "Theoretische Chemie," 5th ed., p. 34.

December 17th, 1910.

I. *The Atomic Theory of Newton.*

In the seventeenth century the atomic theory is associated with the famous names of Francis Bacon (1561—1626), René Descartes (1596—1650), Pierre Gassend (1592—1655), Robert Boyle (1627—1691) and Isaac Newton (1642—1727).

Bacon recurs to the theory again and again in his philosophical writings, as if fascinated by it. At one time he entertained great expectations from the study of the atoms. "I know not whether this inquiry I speak of concerning the first condition of seeds or atoms be not the most useful of all, as being the supreme rule of art and power, and the true moderator of hopes and works."[2] This in the "Cogitationes de Natura Rerum," which is regarded as having been composed before the year 1605. But he changed his mind on the subject, tending, as time passed, to become more and more distrustful of *a priori* reasoning. His mature judgment, as expressed in the "Novum Organum," published in 1620, was that the atoms are an unprofitable study. "Men cease not . . . from dissecting nature till they reach the atom; things which, even if true, can do but little for the welfare of mankind."[3]

Boyle, in this country, was the exponent of the atomic theory who brought it into repute. In the year 1659 he urged the "desirableness of a good intelligence between the Corpuscularian Philosophers and the chemists,"[4] and this topic for some time afterwards he made a leading theme in his scientific writings. Within a few years of his first attempt he was able to say that he has "had the happiness

[2] Bacon's Works, ed. by Spedding & Ellis, vol. 5, p. 423.

[3] *Op. cit.*, vol. 4, p. 68; or *Nov. Org.*, 1, aphorism 66.

[4] Boyle's Works, ed. by Birch, vol. 1, p. 227, 1744.

to engage both divers chymists to learn and relish the notions of the Corpuscular Philosophy, and divers eminent embracers of that to endeavour to illustrate and promote the new philosophy by addicting themselves to the experiments and perusing the books of chemists."[5] While on this subject, he mentions Descartes and Gassend constantly, and other philosophers hardly ever.

Descartes believed in the existence of atoms, and at the same time he denied that a void could exist. A subtle fluid occupied the space between the atoms, and even permeated them. Hence the vortex motion which had been set up in the fluid could not but communicate itself to the atoms. An admirable description of the atmosphere, according to the Cartesian theory, is to be found in Boyle's "New Experiments, Physico-Mechanical, touching the Spring of the Air." "The restless agitation of that celestial matter, wherein these particles [of air] swim, so whirls them round, that each corpuscle endeavours to beat off all others from coming within the little sphere requisite to its motion about its own centre . . . their elastical power is made to depend . . . upon the vehement agitation . . . which they receive from the fluid ether that swiftly flows between them."[6] It is remarkably difficult to find in Descartes so good a description of his theory as this.[7]

Descartes' denial that a vacuum could exist, it is plain from this, is not to be taken in the crudest sense. He never meant and never said that space is full of matter of the ponderable kind.[8] He meant, surely, that in the

[5] *Op. cit.*, vol. 2, p. 501.

[6] *Op. cit.*, vol. 1, p. 8.

[7] Œuvres, ed. by Cousin, vol. 5, p. 159-162, 169-170.

[8] Clerk Maxwell might well have emphasised this in his comment on "The Error of Descartes," in "Matter and Motion," article xvi.

absence of ponderable matter, space is occupied by ether, "the celestial matter;" in short, that "we have no means of producing an ether-vacuum."

A more conventional theory is due to the revival, by Gassend, of the Epicurean philosophy. His interest in this philosophy was such that for twenty years he devoted himself to the study of Epicurus, and Lucretius the Epicurean.[9] Gassend sought to connect the atomic theory with both physical and ethical problems, for those were the days when natural and moral philosophy were studied by the same persons. He brought out three books on the subject, between the years 1647 and 1649, one of which, the "Syntagma Philosophiae Epicuri," was well known to Boyle.

Boyle learnt of the work through his friend Samuel Hartlib, who wrote to him, in a letter dated London, May 9th, 1648: "Your worthy friend and mine, Mr. Gassend, is reasonable well, and hath printed a book of the life and manners of *Epicurus*, since your going from here. He hath now in the press at Lyons the philosophy of *Epicurus*, in which, I believe, we shall have much of his own philosophy, which doubtless will be an excellent work." [10]

There was then, as there is still, a tendency to regard Descartes and Gassend as opponents of one another on the principles of the atomic theory. Boyle mentions some "learned men as more favouring the Epicurean, and others (though but a few) being more inclinable to the Cartesian opinions." However, in one of his essays, he advises *Pyrophilus* to read the "learned *Gassendus*, his

[9] For a study of the Lucretian philosophy, see "Lucretius, Epicurean and Poet," 2 vols., by John Masson. Chap. 1, vol. 2, is devoted to Gassend, of whom it gives a most interesting account.

[10] Boyle's Works, ed. by Birch, vol. 5, p. 257, 1744.

little *Syntagma* of *Epicurus*' philosophy, and that most ingenious gentleman, Mons. *Descartes*, his principles of philosophy."[11] He did not see any necessity to ally himself with one party or the other. "Notwithstanding those things, wherein the atomists and the Cartesians differed, they might be thought to agree in the main, and their hypotheses might, by a person of a reconciling disposition, be looked on . . . as one philosophy."[12]

Science has often gained immensely by a wise limitation of the problem to be solved. Descartes' theory, that space is pervaded by an ethereal fluid, and that ordinary matter consists of atoms swimming in the ether, is formally complete, and has to be adopted sooner or later. Yet Gassend's theory, which is incomplete, since it ignores the ether, and concentrates attention on the atoms, proved more helpful to science in the first instance. Newton was more inclined to Gassend's way of thinking than to Descartes'. In the "Principia" he would not consider the mechanism of gravitation, and in the course of his atomic speculations he almost leaves out of account the means by which chemical attraction arises. Nevertheless, Newton was influenced by Descartes.

The Cartesian natural philosophy was predominant throughout Europe for the most part of the seventeenth century, and, in the eighteenth, it was supplanted by the Newtonian philosophy, as expounded in the "Principia." The two philosophies being opposed to one another, no one apparently has reflected how much Newton may have been indebted to Descartes. The mere fact that Cartesianism was dominant during the seventeenth century means that Newton must have made himself master of that system of nature. Presumably

[11] *Op. cit.*, vol. **1**, p. 194.

[12] *Op. cit.*, vol. **1**, p. 227-228.

then, whatever was sound in Descartes he retained and assimilated. Boyle and Hooke had studied Descartes, and Newton studied all three. In a letter to Hooke, dated Feb. 5th, 1675/6, on the subject of light, he admits his indebtedness to others. "You defer too much to my ability in searching into this subject. What Descartes did was a good step. You have added much several ways, and especially in considering the colours of thin plates. If I have seen further, it is by standing on the shoulders of giants."[13]

Newton, in his speculations on the disintegration of atoms, in Query 31 of the "Optics," had no unusual physical phenomenon in view at the time. He was simply improving on Descartes,[14] whose theory on the subject seems crude enough.[15]

In contrast to the speculative topic of disintegration, another problem which interested Newton was a perfectly concrete one. This was Boyle's law, made known in the year 1662, that the volume of a given quantity of air is inversely proportional to the pressure. Newton's theory of gravitation was based on the assumption that every particle of matter attracts every other particle. In explaining Boyle's law he made the very different assumption that air is composed of particles which repel one another.

This conception of the atmosphere, as being composed of "particles mutually repulsive," was in all probability derived from Descartes. Boyle, in the passage already quoted, where he explains the Cartesian theory, says that in the air, "each corpuscle endeavours to beat off all others from coming within the little sphere requisite to its motion about its own centre."

[13] Brewster's "Life of Newton," vol. 1, p. 142.

[14] Œuvres, ed. by Cousin, vol. 4, pp. 266-268.

[15] I am indebted to my friend, Mr. J. R. Partington, B.Sc., for pointing out to me that Descartes was the source of Newton's ideas on disintegration.

Newton proved that the air must obey Boyle's law, if the force of repulsion between its particles were inversely proportional to the distance between them. He does not mention Boyle, or the air, but puts the matter in the most abstract way, by advancing the following proposition :—"If the density of a fluid which is made up of mutually repulsive particles, is proportional to the pressure, the forces between the particles are reciprocally proportional to the distance between their centres. And *vice versa*, mutually repulsive particles, the forces between which are reciprocally proportional to the distance between their centres, will make up an elastic fluid, the density of which is proportional to the pressure."[16]

Newton does not draw any inference as to the nature of the atmosphere. "All these things are to be understood of particles whose centrifugal forces terminate in those particles that are next them, or are diffused not much further. We have an example of this in magnetical bodies. . . . . Whether elastic fluids do really consist of particles so repelling each other, is a physical question. We have here demonstrated mathematically the property of fluids consisting of particles of this kind, that hence philosophers may take occasion to discuss that question."

This proposition, along with its proof in the "Principia," is the earliest instance of the mathematical treatment of the atomic theory. Svante Arrhenius declares that "the atomic theory remained in the hypothetical state for about 2,300 years, as no quantitative conclusions were drawn from it till the time of Dalton."[17] This statement entirely ignores Newton's explanation of Boyle's law in terms of atoms, as well as certain workers in the eighteenth century, who were under Newton's influence.

[16] "Principia," Book 2, prop. 23.

[17] Arrhenius, "Theories of Chemistry, Eng. trans., p. 15.

II. *Newton's Influence in the Eighteenth Century.*

In the last quarter of the eighteenth century a very remarkable attempt at an atomic theory was made by two Irishmen, by name Bryan Higgins and William Higgins. The object of the second and concluding part of this paper is to show that the theory advanced by Bryan Higgins and amplified by William Higgins can be understood only when regarded as springing, under the peculiar conditions of the time, from Newton's theory. These conditions were (1) the knowledge, due to Priestley, of different kinds of gases, and (2) the new light which Lavoisier threw on chemical composition consequent on Priestley's discovery of oxygen.

The senior of the two men,[18] Bryan Higgins (1737-1820) was self-taught in chemistry, and his career proves him to have been the best all-round man among the English-speaking chemists of his day. His "Experiments and Observations concerning Acetous Acid" (1786) is a record of a very thorough investigation in the field of organic chemistry, in the course of which he discovered the substance acetamide. As a technical chemist his reputation was wide. He spent about four years (1797-1802) in the West Indies, investigating the manufacture of Muscovado sugar and rum. He was a pioneer in the practical teaching of chemistry, and gave instruction in the subject for some twenty-three years (1774-1797) in his *School of Practical Chemistry* in Greek Street, Soho, London. His minor discoveries include that of the musical note which can be got on burning a jet of hydrogen in air (1777).

[18] For fuller information regarding them, see *Brit. Assoc. Rep.*, Dublin meeting, 1908, p. 668, and *New Ireland Review*, 1910, n.s., vol. **32**, pp. and 350-364.

His most important publication, in connection with the atomic theory, is a "Philosophical Essay Concerning Light" (1776). This essay is very different from what it purports to be. It contains only a fragment—all that was ever published—of the essay on light that Higgins had designed. The major part of the book is simply an expansion and exposition of a "Syllabus of Chemistry," which he had published earlier, in 1774 or 1775, and which is also prefixed to the Essay.

Higgins had gone to Newton for inspiration: the "Philosophical Essay" is full of quotations from the "Opticks." Nor need there be any wonder at Higgins making his approach to the study of light by way of chemistry, since Newton's views on chemical subjects are to be found in the "Opticks" more than in any other of his books.

The discovery of new facts always gives a stimulus to speculation. The impulse in Higgins' case came from Joseph Priestley, who showed in the year 1775 that the alkaline substance ammonia, and various acids, hydrochloric, for instance, can exist in the gaseous state. Higgins thereupon proceeded to adapt the Newtonian conception of a gas to the processes of chemistry. Gaseous particles of the same kind were "mutually repulsive," but what should happen in case acid and alkali were brought together? Higgins said that the acid particles and the alkaline attracted one another, and formed a neutral salt by combining *particle with particle.*

Higgins laid great stress on this force of repulsion between particles of the same kind. He thought an acid and an alkali must combine with one another in one proportion only, a combination of two particles of acid and one of alkali, or two of alkali and one of acid, being precluded, because the two similar particles

must repel one another. On this line of thought he finds the answer to his own question:—"Why do many salts crystallise nearly neutral in a liquor containing a superabundant quantity of acid and [*sic*] of alkali?" Further, on the supposition that particles of water and of acid attract one another, as also particles of water and of alkali, he thought he could account for the water of crystallisation found in many salts, so he explains "why much water doth combine in the crystals of most neutral salts, and why this water of crystallisation separates from the superfluous acid or alkali, and introduces little or none of either into the crystals." [19]

In short, on the basis of Newton's theory of a gas, Bryan Higgins taught that chemical combination takes place between acid and alkali in a definite and single proportion. He went little further, if any, with these speculations. His progress must have been greatly hampered by his belief, to which he adhered till about the year 1792, in the phlogiston theory of chemistry, and by his belief in the existence of seven chemical elements, namely, earth, water, air, acid, alkali, phlogiston and light.

William Higgins (1769?-1825) was trained in chemistry by his uncle. He assisted Dr. Beddoes in the teaching of chemistry at Oxford (1787), and acted as chemist to the Apothecaries' Hall of Ireland (1791-1795), and then to the Royal Dublin Society (1795-1825). He was a Fellow of the Royal Irish Academy and of the Royal Society of London.

He did not long suffer from the disadvantages of the phlogiston theory, for he was one of the first to

[19] Bryan Higgins, "A Philosophical essay concerning Light," pp. 201-208, 212-213.

abandon it—in 1785, he says—and was absolutely the first to write against it in the English language. His "Comparative View of the Phlogistic and Anti-phlogistic Hypotheses" (1789) is primarily a refutation of the phlogiston theory. Incidentally, it shows that he had been carrying on experimental work of his own, and also that he had improved on his uncle's speculations. Out of atoms and molecules he fashioned a theory of chemical combination and chemical dynamics as well, so that his book is remarkable as containing the first attempt at a comprehensive system of chemistry, based on the atomic theory.

William Higgins regarded the atom of a gas as a hard particle surrounded by an "atmosphere of fire."[20] He believed firmly that chemical combination occurs in definite proportions, and supposed that it occurs, in the first place, atom with atom. He regarded the molecule of water as formed by the linking of one atom of hydrogen with one of oxygen. "Water is composed of molicules formed by the union of a single ultimate particle of dephlogisticated air to an ultimate particle of light inflammable air . . . they are incapable of uniting to a third particle of either of their constituent particles."[21] In short the formula OH expresses his conception of the molecule of water.

William Higgins was better acquainted with the facts of chemical composition than his uncle, for he did not believe in phlogiston, and he recognised oxygen as one of the elements. He was aware of a number of cases in which elements combine in more than one proportion, and in such cases continued to apply the atomic theory.

[20] "Comparative View of the Phlogistic and Antiphlogistic Hypotheses," pp. 14, 37, 81, 133.

[21] *Ibid.*, p. 37.

He thought an element R must form oxides in the order RO, RO_2, RO_3, etc. Thus he regarded sulphurous acid virtually as SO, and sulphuric acid as SO_2.[22] He recognised five oxides of nitrogen, and regarded them as NO, NO_2, NO_3, NO_4, and NO_5.[23] These ideas of chemical composition are based on the assumption that similar atoms repel one another, an assumption which is also the basis of his system of chemical dynamics. His argument was that because of this force of repulsion, the compound RO is more stable than RO_2, RO_2 than RO_3, and so on.

The line of thought thus opened by the Higginses afterwards proved extremely valuable, but it was not followed up at the time. William Higgins' book, published in 1789, and re-published in 1791, was read as a contribution to the phlogiston and anti-phlogiston controversy. That was the absorbing topic in science then, and nothing else could be duly attended to.

The history of this eighteenth century movement proved a difficult problem in the succeeding century. It occupied the attention at different times of such persons as William Charles Henry, R. Angus Smith, and, in collaboration, Roscoe and Schorlemmer. There was also a long and doubtful controversy regarding the relative merits of William Higgins and John Dalton, the discussion of which is left to a future paper.

Angus Smith's estimate of Bryan Higgins is a vastly different one from that advanced in this paper. His main conclusions are, that Bryan Higgins' "opinions on atoms might have been held by the ancients,"[24] and "that his theory was not clear, or he would have been led by it to

[22] *Ibid.*, pp. 36-37.

[23] *Ibid.*, pp. 132-135, 165.

[24] R. Angus Smith, "Memoir of Dalton," p. 175.

decide on the necessity of fixed composition as a result. But we obtain no results affecting chemical philosophy "[25] In this paper I have shown that Bryan Higgins' theory, far from being "ancient," is a development of Newton's, and that instead of his theory being obscure, and leading to confused ideas regarding chemical composition, it led to a view of the doctrine of fixed proportion, of which the fault was that it was too narrow and rigid.

This difference of opinion, great and hopeless as it may seem, admits of the simplest explanation. Smith's estimate is based upon the "Syllabus" of the year 1775, and upon certain incidental remarks on atoms which he found in the book on "Acetous acid." He was not acquainted with the "Philosophical Essay on Light," which assuredly is not the place where one should expect to find the chemical speculations and ideas regarding atoms, of which nevertheless it is full. Had Angus Smith read this book he must have perceived the clue to the Higgins' ideas, namely, the connection with Isaac Newton. He must then have seen that Bryan Higgins was the first to explain the constant chemical composition of salts in terms of atoms, and that his theory was only too definite and rigid, for it led him to maintain that an acid and an alkali could combine in only one proportion, namely, atom with atom.

W. C. Henry, in his estimate of William Higgins, shows the fatal weakness of failing to see the basis of the theory. Having given Higgins' views regarding the atomic composition of the oxides of nitrogen, he remarks: "It is evident that Mr. Higgins was guided by no fixed and uniform principle, in assigning the atomic constitution of the above compound bodies."[26] This verdict also

[25] *Ibid.*, p. 173.

[26] W. C. Henry, "Memoirs of Dalton," p. 77.

must be set aside. No great penetration of mind is required to divine "the fixed and uniform principle" on which Higgins proceeded in assigning the atomic composition of substances. Although he does not himself mention Newton, there is no room for doubt that Newton's conception of "particles mutually repulsive" was the germ of the theory. Bryan Higgins, who was a student of Newton, made use of this conception, and he communicated it to his nephew. The indebtedness of the nephew to the uncle is as plain as the indebtedness of the uncle to Newton.

There remains now for consideration a remark by Roscoe and Schorlemmer, that "all upholders of an atomic theory" previous to Dalton, "including even [William] Higgins, had supposed that the relative weights of the different elements are the same."[27]

This is a sweeping assertion, of which no proof has ever been offered. One can hardly believe that Newton expressed such an opinion, and it is certain that William Higgins did not. Regarding the oxidation of tin, he supposed that 100 grains of the metal may combine with $7\frac{1}{2}$ or with 15 grains of oxygen.[28] But since he held the oxidation series of an element to be RO, RO_2, RO_3, etc., his figures for tin mean that the atom of the metal was supposed to be much heavier than one atom, or even two of oxygen. Possibly Roscoe and Schorlemmer's statement is based on the case of oxygen and sulphur, which Higgins held to have the same atomic weight. But this conclusion of his depends for one thing on the supposition that the molecule of sulphurous acid (the substance SO_2, not H_2SO_3) is composed of one atom of each element, and for another on

[27] Roscoe and Schorlemmer, "Non-Metallic Elements," p. 35, 1905.

[28] "Comparative View," p. 275.

the experimental fact that the acid is formed by the union of equal weights of the two elements. Higgins proved, quite correctly on his supposition, that the atomic weights of sulphur and oxygen are equal. But proof and assumption are two very different things. Surely it is one thing to prove a result in a particular case, and quite another to assume the result in general.

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V. The Development of the Atomic Theory: (4) Dalton's Physical Atomic Theory.

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In the opinion of the author, many of those who write about Dalton let their attention be engrossed too much by his chemical work. For, in order to understand even the chemical work, it must be kept in mind that Dalton began his scientific career as a meteorologist, that this led him to become a student of physics, and that he took up the study of chemistry subsequently.

The following paper shows that Dalton's physical atomic theory was the first great achievement of his career. It was based on his experimental work, and theory and work together, as soon as published, aroused, in his own words, the "attention of philosophers throughout Europe."

The physical atomic theory, otherwise the theory of "mixed gases," is specially interesting because it marks a stage in the development of Dalton's ideas. Both it and the experiments connected with it arose out of the meteorological observations and studies of his early life. It reveals him as a student of Newton, and as the upholder of a physical atomic theory years before he formed the chemical one.

The present paper is divided into three parts:—I. Dalton's theory of "mixed gases"; II. The beginning and course of Dalton's experimental work; III. The two forms of the physical atomic theory and the dates of their origin.

March 7th, 1911.

I. DALTON'S THEORY OF "MIXED GASES."

The question at issue.

One of the burning questions in science, at the beginning of the nineteenth century, was that of the constitution of "mixed gases." The question could hardly have been discussed much earlier, much less been settled, because the existence of gases, different from atmospheric air and from one another, had not been fully recognised till after the discovery of oxygen in 1774.

The properties of gases are accounted for now by the Kinetic Theory, but this was not established till after the middle of the century. Apart from this theory, men of science explained matters as best they could. The problem naturally arose in connection with the atmosphere, the nitrogen and oxygen of which, although they have different specific gravities, do not separate from one another. Two opinions, says Dalton, arose on this matter: the one supposed the two fluids were "merely mixed together, but assigned no reason why they do not separate . . . . The other supposes a true chemical union to exist between the two, and thus obviates the difficulty arising from the consideration of specific gravity.[1]" The first of these opinions was held by a few isolated individuals. Strange as it must seem now, the chemical explanation of diffusion was not only widespread amongst men of science, but was quite the predominant one.

The germ of Dalton's theory.

Dalton had early shown a tendency in the direction of a mechanical explanation of the state of the atmosphere. The "Meteorological Observations and Essays" published in 1793 contains, as he pointed out many years afterwards,

[1] *Manchester Memoirs*, [1], vol. 5, p. 538, 1802.

"the germs of most of the ideas which I have since expounded more at length in different essays, and which have been considered as discoveries of some importance. For instance, the idea that steam or the vapour of water is an independent elastic fluid . . . . and hence that all elastic fluids, whether alone or mixed, exist independently."[2] He was probably influenced most by Deluc in forming this opinion, but other persons, including Bryan Higgins and Pictet, had expressed views more or less the same as Deluc's.

Dalton's theory of mixed gases.

Thus Dalton had early regarded the constitution of mixed gases from the physical point of view. In the year 1801 he formed a precise theory of his own, which he explained and maintained publicly. The paper in which he describes it, forms one of the set of four experimental essays, which, Dalton himself said, "drew the attention of most of the philosophers of Europe."

He put his theory in the following way: "When two elastic fluids, denoted by A and B, are mixed together, their is no mutual repulsion amongst their particles, that is, the particles of A do not repel those of B, as they do one another."[3] At first the doctrine was not understood, and Dalton had to make further efforts to throw light upon it. His hypothesis meant that while gaseous particles of the same kind repelled one another, there were no forces, whether of repulsion or attraction, between particles of different kinds. Particles of one kind could offer only a passive resistance to the motion of another kind of particles, and acted only as temporary obstacles, in the same way as the pebbles in a stream

[2] "Meteorological Observation and Essays," 2nd Ed., p. v. (1834).

[3] *Manchester Memoirs*, [1], vol. 5. p. 536, 1802.

impede the flow of water. Hence, if two gases were brought together, they were found, sooner or later, to be uniformly mixed.

Dalton and the diffusion of gases.

After the theory had been explained, Dalton deemed it necessary to make new experiments on the diffusion of gases. Priestley, who originally drew attention to this phenomenon, was inclined to think it accidental in its nature. He thought that if "two kinds of air were put into the same vessel with very great care, without the least agitation that might mix or blend them together, they might continue separate."[4] Dalton's experiments, made with the simplest of apparatus, proved, in his own words, "the remarkable fact, *that a lighter elastic fluid cannot rest upon a heavier.*"[5] The importance of this work, by which he established diffusion as a genuine property of gases, was recognised by Berthollet, who carefully repeated it.[6]

Dalton was evidently much gratified by the agreement between his theory and the facts of diffusion. He concludes his memoir on diffusion with a note of triumph :—"The facts, stated above, taken together, appear to me to form as decisive evidence for that theory of elastic fluids which I maintain, and *against* the one commonly received, as any physical principle which has ever been deemed a subject of dispute, can adduce."[7]

Dalton's theory and the vapour of water.

Obviously, a special case of the mixed gases question is that of the water vapour in the atmosphere. The

[4] "Experiments and Observations, &c.," abridged, vol. 2, p. 441.

[5] *Manchester Memoirs*, [2], vol. 1, p. 260, 1805.

[6] *Mém. d'Arceuil*, vol. 2, p. 463, 1809.

[7] *Manchester Memoirs*, [2], vol. 1, p. 270, 1805.

general, though not the universal opinion was, that this vapour was present in a state of combination with the air. The evaporation of water was thought to be an act of chemical combination between air and water, whilst boiling was a physical action. For since the atmospheric pressure prevents water from boiling at ordinary temperatures, it was thought that boiling was something quite distinct from evaporation, which takes place at all temperatures and pressures of the air. This distinction had received the sanction even of Lavoisier.[8]

Dalton's theory had a special bearing on this subject. For the theory meant that the pressure of a mixture of gases is the sum of the respective pressures of the gases in the mixture. Dalton saw that the water vapour in the atmosphere had to be considered in terms of the pressure of the vapour. Experimentally he showed that the evaporation of water is proportional to the pressure of the vapour which the water gives off. At any given temperature there is a maximum which this pressure can reach, and water, whether in contact with the air or not, can evaporate till the pressure of its vapour reaches this maximum and no further. On the other hand, air in which the water vapour is not at this maximum pressure can be cooled till the maximum is reached, and then, on further cooling, the water is deposited as dew. This led to observations of the "dew-point," which Dalton was the first to institute.

It was thus in the direction of Meteorology that Dalton's theory first bore fruit. In this science, as Playfair has pointed out, it is easier than in any other to "accumulate observations, and more difficult to ascertain principles." At the beginning of the nineteenth century, by pointing out the significance of the dew-point, Dalton

[8] "Traité Elémentaire de Chimie," 3rd ed., pp. 7-11, 39.

succeeded in transforming hygrometry, and "raising it to the rank of an exact science."[9]

Dalton's theory and Henry's law.

Dalton's theory had been only a short time before the world, when it was reinforced in a remarkable way. It was found to have an important bearing on the solubility in water of a gas under various pressures. The study of this subject had been undertaken by William Henry, already mentioned in the second paper of this series as a friend of Dalton.

Henry had discovered the law, which is now called after him, that at a given temperature, "water takes up the same volume of condensed gas as of gas under ordinary pressure."[10] The amount dissolved is proportional to the pressure. This, as Dalton pointed out to Henry, is a strong argument in favour of the view that solution is "purely a mechanical effect." If gas, in a state of absorption by water, is retained entirely by the incumbent pressure, there is no need to call in the notion of chemical affinity.

Not only so, but in the matter of the solubility of a mixture of gases, Dalton's theory proved able to sustain a severe enough test. Henry found that each gas dissolved in water as if the others were absent. "Each gas," he concluded, "when dissolved in water, is retained in its place by an atmosphere of no other gas but its own kind."[11] This is precisely what was to be expected from Dalton's theory.

Henry had opposed the theory when it was first made known. He now wrote Dalton a letter, which was read

[9] See W. C. Henry, "Memoirs of Dalton," p. 226.

[10] *Phil. Trans.*, p. 41, 1803.

[11] *Nicholson's Journ.*, [2], vol. 9, p. 126, 1804.

before this Society and then published, expressing his entire satisfaction with it. "In the discussions...which took place in the Society on your several papers, the doctrine of mixed gases was opposed by almost every member interested in such subjects, and by no one more strenuously than myself. I am now satisfied that.... your theory is better adapted than any former one, for explaining the relation of mixed gases to each other, and especially the connection between gases and water."[12]

This support must have been specially gratifying to Dalton, in view of the keen opposition and criticism which the theory was receiving in other quarters. It probably confirmed and enhanced the "almost life-long friendship" between the two men, which is referred to repeatedly in this series of papers.

The "mixed gases" controversy.

The controversy which was aroused by Dalton's theory of mixed gases affords proof at once of the interest taken in his mechanical explanation of the phenomenon, and of the tenacity with which the chemical explanation was adhered to. The view that air is a chemical compound was maintained with a persistency which is hardly credible now, and which throws into relief the originality and vigour of mind which Dalton showed in forming and urging a wiser view. The balance of opinion was against him, for his opponents included Claude Louis Berthollet, Thomas Thomson, John Gough, John Murray, and Humphry Davy.

Dalton's contention, that the diffusion of gases is a physical phenomenon, was at length fully and finally recognised in the Kinetic Theory of Gases. Meantime Dalton had to do his best in the circumstances, and the

[12] *Nicholson's Journ.*, [2], vol. 8, p. 297, 1804.

particular mechanism by which he accounted for diffusion proved specially vulnerable.[13]

The most eager critic of the mechanical explanation was Gough. He wrote numerous letters and essays against it, which were answered by Dalton, and on one occasion by Henry. One of his criticisms was acute. If, as Dalton supposed, the particles of oxygen in the atmosphere have no action on the particles of nitrogen, and *vice versa*, this must affect the transmission of sound. Gough said the oxygen must transmit one sound wave and the nitrogen another, each with its own velocity, so that at a sufficient distance a sound should be heard double.

Berthollet, in his "Essai de Chimie Statique," shows himself a whole-hearted believer in the chemical theory. "It appears to me incontrovertible, that it is a true chemical action which produces the solution of liquids in gases, and evaporation."[14] He was unfavourably impressed by the diagram appended to the "Mixed Gases" Essay, in which Dalton exhibits particles of oxygen, nitrogen, water and carbon dioxide existing in the atmosphere independently of one another.[15] "A diagram in which Dalton has attempted to show how different gaseous molecules may be disposed in the same space, is... only a figment of the imagination."[16]

Thomas Thomson's interest was roused to a high pitch by Dalton's theory. Whilst expressly withholding his assent to it, he noticed it in edition after edition of

[13] As a matter of fact, Dalton did for years believe that "portions of gas of different kinds behave to each other in a different manner from portions of gas of the same kind . . . whereas there is no difference between the two cases." Clerk Maxwell, "Theory of Heat," 10th ed., pp. 28-29.

[14] *Op. cit.*, § 164.

[15] *Manchester Memoirs*, [1], vol. 5, p. 602, 1802.

[16] *Op. cit.*, § 244.

his "System of Chemistry." Dalton's reply to the criticism in the second edition had a notable consequence. Thomson visited Manchester in order to get an explanation of the theory from the author himself, and it was on this occasion that Dalton told him about the chemical atomic theory.

II. The beginning and course of Dalton's experimental work.

The Beginning.

Dalton did not begin original experimental work till 1799, when he was thirty-three years of age, and had been six years in Manchester. Up to then he had confined himself to work of observation, chiefly in meteorology. The first paper in which his own experiments occupy a considerable space is his memoir on the power of fluids to conduct heat. It was read before this Society on the 12th April, 1799.

A previous paper of his, read six weeks earlier, is of quite another stamp. The title of this is as follows:— "A paper, containing Experiments and Observations to determine whether the quantity of Rain and Dew is equal to the quantity of water carried off by the rivers and raised by Evaporation; with an inquiry into the origin of springs." Now, not only are the experiments recorded in this paper hardly worthy of the name, but the subject itself is of the nature of a forlorn hope. Dalton could not have embarked on such a hopeless inquiry as this, if he had been accustomed to experimental research, and had experienced the advantages to be gained simply by limiting the scope of an investigation. This paper, therefore, marks the end of the first stage in his scientific career. By April of the year 1799 he was in the full swing of experimental work.

Experiments connected with the vapour pressure of water.

A paper which Dalton read April 18th, 1800, marks another stage on the way. The title, which is significant of much, runs as follows:—"Experimental Essays, to determine the Expansion of Gases by Heat, and the *maximum* of steam or aqueous vapour, which any gas of a given temperature can admit of; with observations on the common or improved Steam Engines."

On this title four remarks may be made. (1) Dalton had arrived by April, 1800, at the idea, which forms the central fundamental conception of the second and third of the "Experimental Essays" of October, 1801, of the vapour pressure of water. He had begun to consider other gases besides the air, and knew that the maximum of water vapour in any gas is independent of the nature of the gas. It was in order to show this at different temperatures that he began to measure the "expansion of gases by heat."

(2) There is a practical connection between the expansion of gases by heat, and the original topic of the water vapour in the atmosphere. Dalton's explanation of the discrepancies between the results of earlier workers on the subject is that it "arose from the want of due care to keep the apparatus and materials free from moisture."[17]

(3) This paper, although passed for publication by the Society, never appeared. Nothing remains of the "Observations on the common or improved Steam Engines."

(4) Perhaps Dalton had discovered by April, 1800, what we know as Charles' law, that different gases have the same expansion by heat. But he does not make this claim himself. The law forms the subject of the fourth of the "Experimental Essays," and this fourth essay,

[17] *Manchester Memoirs*, [1], vol. 5, p. 596, 1802.

though usually dated October, 1801, was, as a matter of fact, not read then as the first three were before this Society.

Later developments.

Between the paper of April, 1800, and the "Experimental Essays" of October, 1801, Dalton took up the study of only two additional topics. One of these, the vapour pressure of other liquids than water, was a natural outcome of previous work, and calls for no special comment here. The other was that of the explanation of the phenomena of mixed gases. This, a large topic and not an experimental one, is discussed in the last section of this paper. But here is the place to point out that Dalton's reflections on this subject led to two experimental inquiries of the greatest consequence. One of these, already mentioned in this paper, was the study of the diffusion of gases. The other was the determination by Dalton of the composition of the atmosphere, the outcome of which, as will be shown in the next paper, was the formation of the chemical theory.

III. The two forms of the physical theory and the dates of their origin.

The date of the first diffusion hypothesis.

Dalton, in the Introduction to his set of four "Experimental Essays" of October, 1801, explains that this theory of mixed gases was arrived at after his other results. "The first law [*i.e.*, the mixed gases theory] which is as a mirror in which all the experiments are best viewed, was *last* detected, and after all the particular facts had been previously ascertained."[18]

[18] *Manchester Memoirs*, [1], vol. 5, p. 536.

There is no reason to question this statement. It is true that Dalton's historical narratives, as has been shown in the second paper of this series, cannot be accepted at their face value. But this is a contemporary statement, and, as such, must receive a considerable degree of credit.

The physical theory was formed between April, 1800, and September of the following year. There is no hint of it in the title of the paper which Dalton read on the 18th April of the earlier year. Again, the date of the first sketch of the theory, which he sent to *Nicholson's Journal*, is the 14th September, 1801, and the theory can hardly have arisen earlier than August. It is true that Angus Smith assigns the reading of the essay "On the Constitution of Mixed Gases" to July 31st, and October 2nd and 16th for the reading of the 2nd and 3rd essays respectively.[19] But the dates mentioned at the head of the papers in the *Manchester Memoirs*, are the 2nd, 16th, and 30th October. Dalton must have known the dates on which his own papers were read, and as the author he was interested in not dating them later than was necessary. In the Minute-book of the Society the title of each of these papers was entered on a left hand page, and the date and other particulars of the meeting at which the paper was read on the right hand page. Angus Smith has made the slip, which one can easily understand, of assigning the reading of a paper to the meeting minuted on the previous page.

The influence of Newton on Dalton.

The theory was formed under a new influence. Between April, 1800, and August or September, 1801

[19] Angus Smith, "Memoir of Dalton," p. 254. These are not the only wrong dates in his list of Dalton's papers.

Dalton came under the stimulus of Newton's atomic theory. Everything goes to show that this had a great effect on him. He hardly mentions Newton in his early writings. In 1801, and subsequently, he quoted Newton on every suitable occasion, and in particular he mentions the 23rd Proposition of the 2nd Book of the "Principia" at least five times. The mutually repulsive particles of this proposition play their part in Dalton's theory. The wording of it shows this:—"When two elastic fluids, denoted by A and B are mixed together, there is no mutual repulsion amongst their particles; that is the particles of A do not repel those of B, as they do one another."[20]

Dalton's theory is a true development of the theory of Newton, in respect that it is a static one, representing the atoms as being, ultimately, at rest among themselves. If, as was shown in the 3rd paper of this series, Newton in forming his theory deliberately set aside the dynamic ideas of Descartes, it is to be remembered that these ideas at length found expression in the Kinetic Theory of Gases.

The amended diffusion hypothesis.

As already stated in the second paper of this series, Dalton explained in a lecture which he gave in 1810, that he had not at first contemplated the effect of *difference of size* in the particles of elastic fluids. But he reflected that if the sizes be different, then on the supposition that the repulsive power is heat, no equilibrium can be established by particles of different sizes pressing against each other." On consideration, he found "that the *sizes must* be different;" "thus," he concludes, "we arrive at the reason for that diffusion of every gas through every other gas,

[20] *Manchester Memoirs*, [1], vol. 5, p. 536, 1802.

without calling in any other repulsive power than the well known one of *heat*." This, he says, occurred in 1805.[21]

In later life, Dalton gave up this amended hypothesis, and reverted to his original one.[22] But in 1808 he expounded them both in the "New System." This may seem inconsistent of him, inasmuch as the two hypotheses are different from one another. Yet they are both forms of the physical atomic theory. Dalton's consistency lies in his adherence to a mechanical hypothesis in contrast to a chemical one. The question of the precise mechanism was subsidiary, and the mixed gases controversy turned entirely on the theory which Dalton advanced in 1801. No one took any notice of his change of front. It has, therefore, not been necessary to consider the amended diffusion hypothesis till now. The hypothesis is less important for its own sake than in its bearing, or supposed bearing, on the development of Dalton's chemical theory.

The amended hypothesis and the chemical atomic theory.

In the lecture already quoted, Dalton connects this amended hypothesis with the genesis of his chemical atomic theory. "The different *sizes* of the particles of elastic fluids under like circumstances . . . . being once established, it became an object to determine the relative *sizes* and *weights* together with the relative *number* of atoms in a given volume. This led the way to the combination of gases . . . . Thus a train of investigations was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination with one another."[23]

[21] Roscoe and Harden, "New view of the origin of Dalton's Atomic Theory," pp. 16-17.

[22] *Phil. Trans.*, 1826, part 2, p. 174.

[23] Roscoe and Harden, *loc. cit.*

"This led the way to the combination of gases." Undoubtedly the combination of gases was the basis of Dalton's chemical theory, and the gist of his narrative is, that he *first* concluded the particles of different gases to be different in size, and *subsequently* arrived at his chemical theory.

1805 or 1803?

Roscoe and Harden, instead of taking this narrative as a document requiring interpretation in the light of the available information, and above all, in the light of Dalton's habit of mind, have accepted it at its face value. Even then they are compelled to admit there is something wrong. The note-books shew that the chemical theory was formed in 1803, and if the amended diffusion hypothesis was formed previously, then the date, 1805, which Dalton gives, must be wrong. Roscoe and Harden conclude that the date of the amended hypothesis is 1803.[24]

The date is 1804.

There are two grave objections to the supposition that the theories were formed in the order given by Dalton. One of these is based on the nature of the theories, and will be considered in the next paper. The other has to do with the genesis of the diffusion hypothesis. Roscoe and Harden have failed to quote from the note-book the passage which deals with this. It is as follows:—

"*On the ultimate atoms of elastic fluids.*

"There are but three positions that are any way likely to be true on this head.

"1. The ult. atoms of all gases are of the same weight.

[24] *Op. cit.*, p. 25.

"2. The ult. atoms are of the same relative weight as the gases themselves.

"3. That neither of these positions is accurate.

"According to the first the gases of greatest specific gravity are those whose particles are closest and the diameters of the elastic particles will be as the cube root of the sp. gr. This cannot be true for nit. gas which is made up of azot and oxygen is lighter than oxygen itself; and so is aq. vapour than oxygen one of its constituents."[25]

"According to the 2nd position all gases will have the same number of particles, and consequently the same distances of each in a given volume, under like circumstances. This position is contradicted by facts: for all compounds would be heavier than their simples upon this principle, which is contrary to experience.

"The two former positions being disproved, it follows that when two gases of like force, &c., are presented to each other, the number of particles in a given surface of one of them will not be the same as in the other; consequently, no proper equilibrium can take place."[26]

This material is as important as anything on the subject can well be. The pages quoted, Nos. 109 and 111 of the note-book, amount to a summary of Dalton's reasoning on the subject of the sizes of atoms, leading to his decision in favour of the new diffusion hypothesis. It is easy to assign a date to this decision. By reason of the subject-matter, pages 107, 109, and 111 are closely connected with one another. Page 107 contains a table of the weights and diameters of atoms, a table which, it may well be supposed, was drawn up in order to illustrate Dalton's inquiry into the sizes of atoms. It is dated

[25] Note-books, vol. 1, p. 109.

[26] *Op. cit.*, p. 111.

September 14th, 1804, and this is the approximate date of the amended diffusion theory.

Dalton probably influenced by Thomson and Gough.

Up to this time Dalton had given no sign of anything but the fullest confidence in his original theory. He had defended it eagerly, and, as late as June, had been encouraged in his belief by the accession of William Henry to his side. What then could have induced Dalton, not a very impressionable man, to reconsider the matter?

It may be assumed, in the absence of any positive information on the subject, that the change was due partly to Thomas Thomson and partly to John Gough. As has already been mentioned more than once in these papers, Thomson visited Manchester with the express object of discussing the mixed gases theory with Dalton. Now everything goes to show that Thomson made a considerable impression on him and won his confidence. He explained the chemical theory to Thomson in detail, and afterwards mentioned Thomson's opinions regarding mixed gases, although adverse to his own, with the utmost respect.[27] Consequently one can well believe that Thomson's scepticism regarding the original mixed gases theory began to shake his confidence in it. Again, John Gough had written two letters, which appeared in *Nicholson's Journal*, criticising the theory. The criticism was effective, for Dalton, although he continued to maintain his theory, made no answer at the time to Gough's argument regarding the velocity of sound. Gough's letters are dated July 16th and August 23rd, 1804, respectively. The interview between Dalton and Thomson occurred on

[27] "New System of Chemical Philosophy," 1808, p. 72.

the 27th August, and Dalton's reply to Gough is dated 8th September. Thus Thomson's objections to the theory, with Gough's in addition, may have compelled Dalton to reconsider the matter. There was time for reconsideration between the 8th September and the 14th, the date of Dalton's decision to put the explanation of the diffusion of gases on a new basis.

The principal references connected with the theory of mixed gases.

1792.

1. "On Evaporation," by JEAN ANDRÉ DELUC. *Phil. Trans.*, p. 400.

1793.

2. "Meteorological Observations and Essays," by JOHN DALTON.

1799.

3. "Experiments and Observations, to determine whether the quantity of Rain and Dew is equal to the quantity of Water carried off by the rivers and raised by evaporation; with an Inquiry into the Origin of Springs," by JOHN DALTON. Read* March 1st. Pub. *Manchester Memoirs*, vol. 5, part 2, p. 346, 1802. (The footnote, p. 351, was added after the paper was read.)

1800.

4. "Experimental Essays, to determine the Expansion of Gases by Heat, and the maximum of Steam or Aqueous Vapour, which any Gas of a given temperature can admit of; with observations on the common and improved Steam Engines," by JOHN DALTON. Read April 18th. Never published in full; see no. 8.

* In the above list, "read" means read before the Manchester Literary and Philosophical Society.

1801.

5. "New theory of the constitution of mixed aeriform fluids, and particularly of the atmosphere," by JOHN DALTON. Written September 14th. Pub. *Nicholson's Jour.*, [1], vol. 5, p. 241.

6-9. "Experimental Essays on the Constitution of mixed gases; on the force of steam or vapour from water and other liquids in different temperatures, both in a torricellian vacuum and in air; on evaporation; and on the expansion of gases by heat," by JOHN DALTON. The 1st of these four essays was read Oct. 2nd, the 2nd Oct. 16th, the 3rd Oct. 30th. Pub. *Manchester Memoirs*, [1], vol. 5, p. 535, 1802.

1802.

10. "System of Chemistry," by THOMAS THOMSON, 1st ed., vol. 3, p. 270.

11. "New theory of the constitution of mixed gases elucidated," by JOHN DALTON. Written Nov. 18th. Pub. *Nicholson's Jour.*, [2], vol. 3, p. 267. (Chiefly called forth by no. 10.)

12. "Experimental Inquiry into the Proportion of the several gases or elastic fluids constituting the atmosphere," by JOHN DALTON. Read Nov. 12th. Pub. *Manchester Memoirs*, [2], vol. 1, p. 244, 1805.

1803.

13. "Essai de Chimie Statique," by C. L. BERTHOLLET (especially §§ 158, 160, 163, 164, 171, 240, 242—244).

14. "On the tendency of elastic fluids to diffusion through each other," by JOHN DALTON. Read Jan. 28th. Pub. *Manchester Memoirs*, [2], vol. 1, p. 259, 1805.

15. "On the absorption of gases by water and other liquids," by JOHN DALTON. Read Oct. 21st. Pub. *Manchester Memoirs*, [2], vol. 1, p. 271, 1805.

16. "An Essay on the theory of mixed gases and the state of water in the atmosphere," by JOHN GOUGH. Read Nov. 4th. Pub. *Manchester Memoirs*, [2], vol. 1, p. 296, 1805.

17. "A reply to Mr. Dalton's objections to a late theory of mixed gases," by JOHN GOUGH. Written Dec. 2nd. Read Jan. 27th, 1804. Pub. *Manchester Memoirs*, [2], vol. 1, p. 405, 1805.

18. "Appendix to Mr. WILLIAM HENRY'S paper, on the quantity of gases absorbed by water, at different temperatures, and under different pressures." *Phil. Trans.*, p. 274.

1804.

19. "System of Chemistry," by THOMAS THOMSON, 2nd ed., vol. 3, p. 316.

20. "On the supposed chemical affinity of the elements of common air; with remarks on Dr. Thomson's observations on that subject," by JOHN DALTON. Written June 16th. Pub. *Nicholson's Jour.*, [2], vol. 8, p. 145. (A reply chiefly to no. 19.)

21. "Illustration of Mr. Dalton's theory of the constitution of mixed gases," in a letter from Mr. Wm. Henry, of Manchester, to Mr. Dalton. Written June 20th, read June 29th. Pub. *Nicholson's Jour.*, [2], vol. 8, p. 297.

22. "On the solution of water in the atmosphere, and on the nature of atmospherical air," by JOHN GOUGH. Written July 16th. Pub. *Nicholson's Jour.*, [2], vol. 8, p. 243.

23. "Strictures on Mr. Dalton's doctrine of mixed gases, and an answer to Mr. Henry's defence of the same," by JOHN GOUGH. Written Aug. 23rd. Pub. *Nicholson's Jour.*, [2], vol. 9, p. 52. (A reply to nos. 20 and 21.)

24. "Observations on Mr. Gough's strictures on the doctrines of mixed gases, &c.," by JOHN DALTON. Written Sept. 8th. Pub. *Nicholson's Jour.*, [2], vol. 9, p. 89. (A reply to nos. 22 and 23.)

25. "Atmospherical air not a mechanical mixture of the oxigenous and azotic gases, demonstrated from the specific gravities of these fluids," by JOHN GOUGH. Written Sept. 5th. Pub. *Nicholson's Jour.*, [2], vol. 9, p. 107.

26. Letter to the Editor from Mr. William Henry in reply to Mr. Gough. Written Sept. 13th. Pub. *Nicholson's Jour.*, [2], vol. 9, p. 126. (In reply to nos. 22 and 23.)

27. "Reply to Mr. Dalton on the constitution of mixed gases," by JOHN GOUGH. Written Oct. 16th. Pub. *Nicholson's Jour.*, [2], vol. 9, p. 160. (A reply to no. 24.)

28. "Observations on Mr. Gough's two letters on mixed gases," by JOHN DALTON. Written Nov. 15th. Pub. *Nicholson's Jour.*, [2], vol. 9, p. 269 (in reply to nos. 25 and 27).

29. "Further observations on the constitution of mixed gases," by JOHN GOUGH. Written Dec. 13th. Pub. *Nicholson's Jour.*, [2], vol. 10, p. 20, 1805.

1805.

30. "Remarks on Mr. Gough's two Essays on Mixed Gases, and on Professor Schmidt's experiments on the expansion of dry and moist air by heat," by JOHN DALTON. Read Oct. 4th. Pub. *Manchester Memoirs*, [2], vol. 1, p. 425 (a reply to nos. 16 and 17).

1806.

31. "System of Chemistry," by JOHN MURRAY. Vol. 2, pp. 48-53, and note E.

1807.

32. "System of Chemistry," by THOMAS THOMSON. 3rd ed., vol. 3, p. 440.

33. "On the Chemical composition of the Atmosphere." Works, vol. 8, pp. 252-255, by HUMPHRY DAVY.

1808.

34. "New System of Chemical Philosophy," by JOHN DALTON, pp. 150-208.

1809.

35. "Experiments on the expansion of moist air raised to a boiling temperature," by JOHN GOUGH. Written May 22nd. Pub. *Nicholson's Jour.*, [2], vol. 23, p 182.

36. "Sur le mélange réciproque des gaz," par C. L. BERTHOLLET. *Mém. d'Arceuil*, vol. 2, p. 463 (a repetition of Dalton's experiments in no. 14).

1826.

37. "On the constitution of the Atmosphere," by JOHN DALTON. *Phil. Trans.*, part 2, p. 174.

1837.

38. "Sequel to an Essay on the constitution of the Atmosphere," by JOHN DALTON. *Phil. Trans.*, p. 347.

1834.

39. Dr. Prout's reply to Dr. W. Charles Henry. Written July 18th. *Phil. Mag.*, [3], vol 5, p. 133.

1844.

40. "Observations on the Diffusion of Gases," by T. S. THOMSON. *Phil. Mag.*, [3], vol. 25, p. 51.

1842.

41. "Elements of Chemistry," by THOMAS GRAHAM, pp. 69, 70, 71, 75.

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VI. The Development of the Atomic Theory: (5) Dalton's Chemical Theory.

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Introduction.

In the year 1801 Dalton's physical atomic theory (described in the fourth paper of this series) was devised as an explanation of the diffusion of gases. Since the prevailing tendency of the time had been to regard diffusion as due to chemical affinity between the gases concerned, Dalton was forced to consider carefully the nature of physical and chemical changes, and to draw a distinction between them. His own theory of diffusion turned on this distinction. Thus, in the course of his argument against the supposition that diffusion is due to chemical affinity, he asks the question, "Why do not oxygenous and azotic gases, taken in due proportion and mixed, constitute nitric acid gas, another elastic fluid, totally distinct in its properties, from either of the ingredients."[1] Obviously, therefore, whilst Dalton's attention was being directed *principally* to physical phenomena, he had in his mind a distinct conception of chemical change.

The object of this paper is to consider how Dalton passed from the physical atomic theory, which was formed first, to the chemical one, which was formed afterwards. The author has already shown, in the second paper of this series, that the various narratives we possess of the origin of the chemical theory, can be traced back to

[1] *Manchester Memoirs*, vol. 5, pp. 538-539, 1802.

Dalton himself. This is simply what was to be expected in the nature of the case. Moreover, since Dalton was inconsistent in the matter, no single account of his can be accepted at its face value. The version of the origin which is advanced in this paper, consequently, need not be rejected off-hand, as not having received the sanction of Dalton. It is offered as a fair account of the present state of our knowledge, on a matter on which absolute certainty is not yet attainable.

The paper is divided into two parts :—I. The principles of Dalton's theory ; II. The genesis of the theory.

I. The principles of Dalton's theory.

The first table of atomic weights.

For the present purpose of studying the origin of the chemical theory, Dalton's note-books contain material of inestimable value: they afford facts which cannot be disputed. Under date 6th September, 1803, there is an atomic weight table of the highest interest. It is quoted by Roscoe and Harden as follows :—*

Ult. at. hydrogen	1
„ „ oxygen	5·66
„ „ azote	4
„ „ carbon	4·5
„ „ water	6·66
„ „ ammonia	5
„ „ nitrous gas... ...	9·66
„ „ „ oxide ...	13·66
„ „ nitric acid	15·32
„ „ sulphur	17
„ „ sulphurous acid ...	22·66
„ „ sulphuric „ ...	28·32
„ „ carbonic „ ...	15·8
„ „ oxide of carbon ...	10·2

* "New View of the Origin of Dalton's Atomic Theory," p. 28.

This table of atomic weights is of extraordinary interest because, besides being the earliest known, it is based on the same ideas as the one published in the "New System" five years later. There is only one change: sulphurous and sulphuric acids in the earlier table are virtually SO and SO_2 respectively, and in the later table they are SO_2 and SO_3. But this does not affect the fact that after the table was drawn up in 1803, Dalton made no essential change in the theory. The principles of 1803 remain as nearly as possible unchanged in 1808, so far as one can judge of principles by results. In the one scheme just as in the other, the compound atom of water consists of 1 atom of hydrogen and 1 of oxygen, that of ammonia of 1 of hydrogen and 1 of nitrogen. Nitrous gas is virtually NO, nitric acid is NO_2, nitrous oxide N_2O, carbonic oxide is CO, carbonic acid is CO_2.

Debus on the "Dalton-Avogadro" hypothesis.

Debus has devoted a series of papers to the study of the principles on which Dalton arrived at chemical formulæ and atomic weights. The whole series may be said to depend on the assumption that Dalton deliberately made a mystery of the evolution of his theory. "Der geniale Baumeister hat sorgfältig alle Werkzeuge und Pläne entfernt und zeigt ohne einleitende Bemerkungen sofort das fertige Gebäude."[2] This is the kind of statement which ought not to be made except as the result of an exhaustive study of the available material. Everyone must admit that the subject is obscure, but, as will appear in the course of this paper, there is little justification for saying that Dalton deliberately (sorgfältig) made it so. The true explanation of the obscurity is that the task of

[2] *Zeitsch. physik. Chem.*, 1899, vol. 29, p. 266.

considering how his own ideas had arisen was uncongenial to him, and he never devoted his mind to it.

As the result of his studies, Debus concluded that Dalton was greatly influenced, during the development of his atomic theory, by the supposition that the particles of different gases under similar conditions are of the same size. This doctrine, which is usually known as Avogadro's hypothesis, Debus calls the "Dalton-Avogadro" hypothesis.

Debus first advanced this belief of his in a pamphlet entitled, "Ueber einige Fundamentalsätze der Chemie, insbesondere das Dalton-Avogadrosche Gesetz" (1894, Cassel). His opinion having been controverted by Roscoe and Harden, in their "New View of the Origin of Dalton's Atomic Theory," he replied, and a controversy ensued, in which G. W. A. Kahlbaum also took part. The series of papers is as follows:—Debus, *Zeitsch. physikal. Chem.*, vol. 20, p. 359, 1896 (or *Phil. Mag.*, vol. 42, p. 350, 1896); Roscoe and Harden, *Zeitsch. physikal. Chem.*, vol. 22, p. 241, 1897 (or *Phil. Mag.*, vol. 43, p. 153, 1897); Debus, *Zeitsch. physikal. Chem.*, vol. 24, p. 325, 1897; vol. 29, p. 266, 1899; Kahlbaum, *Zeitsch. physikal. Chem.*, vol. 29, p. 700, 1899; Debus, *Zeitsch. physikal. Chem.*, vol. 30, p. 556, 1899.

Debus can justify his belief in two ways:—(1) Dalton certainly stated in 1808 that he once had a sort of belief in the hypothesis in question. "At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous; or if not, that we have no data from which the question could be solved. But . . . .

I became convinced that different gases have *not* their particles of the same size."[3]

(2) Debus argues, from a phrase in Thomas Thomson's first sketch of the atomic theory, that Dalton was still in 1804 a believer in the hypothesis. This is the phrase, "the density of the atoms."

The "density of the atoms."

The interpretation of this phrase is open to question, and Roscoe and Harden do not agree with Debus on the matter. But neither they nor any of the parties to the controversy seem to be aware that Dalton put exactly the same construction on the phrase as Debus, and at the same time repudiated the opinion which it attributed to him. "It is rather amusing to me to observe the different manners in which a cursory view of the atomic system strikes different observers. Dr. Thomson . . , used the phrase *density of the atoms* indifferently for *weight of the atoms*, thereby implying that all atoms are of the *same size*, and differ only in *density;* but he has since very properly discontinued the use of the phrase."[4]

It is, of course, impossible that a statement, made by Dalton in 1814, can be taken to prove that he did not use a misleading expression in a conversation held ten years earlier. He may have used the phrase in question in his interview with Thomson, or Thomson may have originated the phrase. These are the two possibilities. But the matter is not one of high importance. There are far stronger arguments than this statement of the year 1814 can be, against the opinion held by Debus.

[3] "New System of Chemical Philosophy," 1808, pp. 187-188.

[4] *Ann. of Phil.*, vol. 3, p. 175, 1814.

Dalton practically ignores the hypothesis.

The really important question is, the sense in which Dalton held this hypothesis. Did he perceive and consider all its consequences, immediate and remote, and did he, in any way, act upon his belief in it? That he did none of these things is the plain meaning of the passage in which he speaks of his holding the hypothesis as a "confused idea."

There are four different ways in which Dalton might have applied the hypothesis, or drawn deductions from it:

1. The hypothesis is to the effect that particles of nitrogen and oxygen are of the same size. Dalton's first explanation of diffusion was that particles of oxygen neither attract nor repel those of nitrogen. Between these two opinions there is no necessary connection. He did not hold the diffusion theory as a logical consequence of the hypothesis, and he did not even specify the hypothesis in his explanation of the theory.

2. Dalton did not use the hypothesis as a means of arriving at atomic weights and formulæ. He used for that purpose the 1 : 1 rule, which led him to the formula OH for water, whilst the hypothesis must have led to the formula H_2O. Thomson, in his first sketch of the theory, says expressly that the 1 : 1 rule was "the hypothesis on which the whole of Mr. Dalton's notions . . . is founded."[5]

3. What is known as Gay-Lussac's law, regarding the combining volumes of gases, is a necessary consequence of the hypothesis. This everyone must admit. Yet Dalton did not at once deduce the law from the hypothesis, and when at length he did so, and endeavoured to test it experimentally, he regarded his results as dis-

[5] "System of Chemistry," 3rd edition, 1807, vol. 3, p. 424.

proving both doctrines. Debus, as the author has pointed out elsewhere, has committed himself to the opinion that Dalton could be at one and the same time a believer in the hypothesis and not in the law.[6]

4. Finally, Dalton held this hypothesis without considering that it leads to the conclusion, familiar now to chemists, that the "atoms" of hydrogen, oxygen and other elements are divisible.

There is no evidence, not the faintest indication, that Dalton had realised the hypothesis before the end of the year 1803, in any one of these four ways. It is, therefore, impossible to suppose that the hypothesis—the "confused idea"—had any influence on him whilst he was forming his chemical atomic theory.

The main principles of Dalton's system.

The principles on which Dalton based his theory must have continued the same from 1803 to 1808, simply because his opinions regarding the "atom" of water, of ammonia, etc., remained the same. The general principles regarding the combination of atoms, which he set out in 1808, are somewhat cumbrous, and some of them superfluous. They can be reduced to two:—(1) That atoms of different kinds tend to combine in the proportion 1 : 1 rather than in any other, that the next proportion to occur is 1 : 2, then 1 : 3, and so on ; (2) that when two compounds of the same two elements are gaseous, the lighter is binary and the heavier tertiary.

It is true that this second principle is not to be found among the set of rules which Dalton gives in the "New System of Chemical Philosophy." He says there that

[6] "Avogadro and Dalton—the standing in Chemistry of their hypotheses," 1904, pp. 63-66.

"a binary compound should always be specifically heavier than the mere mixture of its two ingredients" [compounds and ingredients being supposed to be gaseous]. This rule is open to two objections:—(1) It is not true, as the case of hydrochloric acid shows; (2) it is of no use and was not used for the problem that Dalton had to solve. It cannot be used to ascertain whether the two gaseous oxides of carbon ought to receive the formulæ CO and CO_2 respectively, or C_2O and CO. In the 2nd part of the "New System" he says:—"carbonic acid is of greater specific gravity than carbonic oxide, and on that account it may be presumed to be the ternary or more complex element [*sic*]. It must, however, be allowed that this circumstance is rather an indication than a proof of the fact."[7] One can well believe that it was on this principle Dalton arrived at the molecular constitution of these gases, and of nitric and nitrous oxides as well, in the year 1803.

The connection between the physical and the chemical theories.

The first rule has been called the rule of "greatest simplicity," not only in allusion to its character, but as meaning that it is based on the instinct for simplicity and needs no other justification. As a matter of fact Dalton deduced it from first principles. Dr. Bostock, in the course of a criticism of the atomic theory, raised the question, "When bodies unite only in one proportion, whence do we learn that the combination must be binary?"

In answer Dalton gave an explanation, which shows that Newton's postulate of similar particles, which are "mutually repulsive," was the fundamental idea of the

[7] "New System of Chemical Philosophy," 1810, p. 369.

chemical as it had been of the physical atomic theory. "When an element A has an affinity for another B, I see no mechanical reason why it should not take as many atoms of B as are presented to it, and can possibly come into contact with it, . . . except in so far as the repulsion of the atoms of B among themselves are [*sic*] more than a match for the attraction of an atom of A. Now this repulsion begins with 2 atoms of B to 1 of A, in which case the 2 atoms of B are diametrically opposed; it increases with 3 atoms of B to 1 of A, in which case the atoms of B are only 120° asunder . . . . and so on in proportion to the number of atoms. It is evident then from these positions, that, as far as powers of attraction and repulsion are concerned (and we know of no other in chemistry) . . . *binary* compounds must first be formed in the ordinary course of things, then *ternary* and so on, till the repulsion of the atoms of B . . . refuse to admit any more."[8]

Consequently, Newton's postulate of similar particles which are mutually repulsive, is the basis of both the physical and the chemical atomic theories of Dalton.

II. The Genesis of the Chemical Theory.

The inductive and deductive accounts of the genesis.

This discussion of principles, however, does not exhaust the subject. Much remains obscure regarding the train of thought which Dalton followed in passing from the physical to the chemical theory. The crucial question is, how he arrived at, what suggested, the doctrine of combination of atoms in multiple proportion?

Two main accounts of the origin of the theory have

[8] *Nicholson's Jour.*, vol. 29, p. 147, 1811; see also "New System of Chemical Philosophy," vol. 1, p. 216, 1808.

been offered. They have already been mentioned in the second paper of this series. The first of these, coming direct from Thomas Thomson, is that Dalton discovered the composition of marsh gas and olefiant gas and was led thereupon to perceive the law of multiple proportions, and to devise his chemical theory as an explanation of the law. This may be called the *inductive* account.

Again, Roscoe and Harden accept an account, offered by Dalton, which may be called the *deductive* one. Dalton had formed his diffusion hypothesis without considering the "effect of *difference of size* in the particles of elastic fluids." On consideration he found that "the *sizes must* be different," and thereupon he revised his diffusion theory. He then introduces the subject of the chemical theory :— "The different *sizes* of the particles of elastic fluids .... being once established, it became an object to determine the relative *sizes* and *weights*, together with the relative *number* of atoms in a given volume. This led the way to the combination of gases," etc.

Objections to the purely inductive and deductive accounts.

There being these two accounts, the inductive one and the deductive, of the origin of the theory, there arises the question, which comes nearer the truth? The Board of Education has recently committed itself to an opinion on this topic, in the course of its criticisms on the answers of students to its questions on chemistry. The particular question was :—"Give a short account of Dalton's atomic theory, and discuss its value in explaining the laws of chemical combination."

Teachers of chemistry, to judge from the reference made to them, have been adopting Roscoe and

Harden's view of the matter. "... The teachers are to blame ... in allowing so many of their students to put the "cart before the horse" as they do in connection with the atomic theory. The idea seems to prevail that the laws of chemical combination follow from the atomic theory, whereas the laws of combination were established first as the results of experiments, and the atomic theory of Dalton provides an explanation of the facts."[9]

It is, of course, begging the question to assume that the matter is as simple as this. Everyone knows which is the cart and which is the horse, and no one knows for certain how Dalton's chemical theory arose. Again, one may urge, that supposing the origin of the theory to be a controversial matter, the Board of Education is not called upon to take one side or the other, and indeed, might well avoid such topics in its examination papers.

The matter, however, is no longer controversial, being so far settled that the purely inductive view of the origin is quite untenable. There is the objection to it in principle, that it says nothing about Dalton's physical theory to which W. C. Henry drew attention long ago, and Roscoe and Harden recently. Besides, Roscoe and Harden have advanced objections to it in detail, which must be final to anyone who considers them.[10]

Reasons must now be offered for rejecting the deductive account which Roscoe and Harden have accepted. The gist of it is that Dalton *first* satisfied himself that the atoms of different gases have different sizes, and *then* devised the chemical theory. This, Dalton's own narrative, has already been quoted on p. 10. He gave it seven years after the events which it relates, and it is quite unsatisfactory. It does not condescend to

[9] "Science Examinations," 1909, p. 119. Board of Education.

[10] "New View of the Origin of Dalton's Atomic Theory," p. 28.

particulars and instances. Dalton does not explain, nor is it obvious that anyone can explain, how he was to test the sizes of atoms without some kind of chemical theory. One may either *assume* that different atoms have the same size, and act accordingly, or one can endeavour to test the position, by obtaining data regarding atoms, on the basis of some hypothesis as to the way in which they combine chemically.

It has been shown in this paper that Dalton, so far as the formation of the chemical theory is concerned, did not act on the belief that atoms of different kinds have the same size. Again, the author has already shown, in the paper on Dalton's physical atomic theory, that the chemical theory was formed first and the conclusion that "atoms" of different gases were different in size was come to afterwards.

This is the order that was to be expected in the nature of the case. Moreover, there is nothing in the note-books to show that the chemical theory was devised except for its own sake. The testing of the sizes of atoms was an afterthought. The connection between the sizes of atoms and the diffusion of gases was not considered till a year after the chemical theory had been formed.

The experiments of August 4th, 1803.

The chief matter that continues to be doubtful is the exact way in which Dalton arrived at the law of multiple proportion. The author, after a careful consideration of the evidence, can come to no other conclusion than that it was Dalton's experiments on the combination of nitric oxide and oxygen that aroused his attention, and made him apply his physical theory to the purposes of chemistry.

The facts, as established by the note-books, are that Dalton, for the purpose of his inquiry into the composition of the atmosphere, was studying the combination of nitric oxide and oxygen in the year 1803. He was at work on the subject during March and April, and then again in August. On the 4th of August he obtained the well-known result that 100 measures of air could take 36, or 72, of nitric oxide.[11] His first table of atomic weights was drawn up by the 6th of September.

The first case of combination in multiple proportions observed by Dalton must have seemed of great importance to him. His observation of August 4th, regarding nitric oxide and the oxygen of the air, is the first of the kind which he recorded. It is difficult to suppose that he can have known an earlier one. Yet Roscoe and Harden think that this case was of comparative unimportance in the development of the atomic theory. Their reason is that the chemical compounds concerned are not sufficiently represented in the first table of atomic weights. The chemical changes, as Dalton understood them, may be set out in the equations :—

(1) $NO + O = NO_2$ (nitric acid).
(2) $2NO + O = N_2O_3$ (nitrous „).

Certainly, if the whole matter turned on nitrous acid, Roscoe and Harden argue, it is surprising that Dalton ignored this substance in making up his table on September 6th. They suggest that the symbol for nitrous acid which appears at the side of the table was added afterwards, probably about the 12th October. Everyone must admit this who inspects the original table, or the photograph in Roscoe and Harden's book.

Dalton seems to have set aside the case of nitrous acid

[11] Roscoe and Harden, *op. cit.*, pp. 34, 38.

for a time as being too complicated. The union of two atoms of one kind with three of another must have appeared at that stage of thought to be very complex. Dalton did not adopt such a formula till October. On the 12th of that month, as a summary of his views, he gives tables of binary compounds, of ternary, of compounds of 4 atoms, and compounds of 5. Alcohol and nitrous acids were the only compounds of 5 atoms. Alcohol is ether and water united, or 2 oxygen, 2 carbon, and 1 hydrogen. Nitrous acid is 3 oxygen and 2 nitrogen.

The objection of Roscoe and Harden, however, must be final, but for one circumstance: the objection ignores the physical theory. The experiments with nitric oxide and air must have received lengthy consideration had it not been for the fact that Dalton had an atomic theory already in his mind. As it was, these experiments simply served to give the impulse needed to set his mind working. Under that stimulus he made a beginning with the adaptation of the physical theory to chemical purposes.

Nothing more was needed. Larmor, in his *Wilde Lecture* on the "Physical Aspect of the Atomic Theory," represents that the doctrine of combination of atoms in the proportion 1 : 1 must forthwith lead to other cases such as 1 : 2.

"Once it is postulated that only one kind of aggregation into molecules occurs, *e.g.*, that in water there is only one way in which the hydrogen attaches itself to the oxygen, the laws of definite and multiple proportions are self-evident."[12]

Earlier in this paper, the author has pointed out how the doctrine of 1 : 1 arose logically from the physical theory. There are here, therefore, all the elements of a fair account of the origin of Dalton's chemical theory.

[12] *Manchester Memoirs*, vol. 52, no. 10, p. 9. 1908.

The germ of it is to be found in Newton's theory and in Dalton's physical theory of the year 1801, and one must recognise the space of two years during which it remained in the germ. There comes then the experiment of the 4th of August, 1803, sufficient to arouse Dalton's attention and make him apply his theory to the purposes of chemistry. He frames the rule of 1 : 1, then considers the less simple cases, and tests his ideas by the available analytical data. By the 6th of September he is able to draw up the first atomic-weight table.

Chemistry without the atomic theory.

Attempts have been made in recent years, by Wald and Ostwald, to deduce the laws of chemical combination from first principles, without making any use of the atomic theory.[13] It seems to the author worth pointing out here that there is no connection between the modes of thought taken by these writers, and the process by which these laws were actually established. With the atomic theory as a starting point, they were formulated by Dalton and completely established by Berzelius. Moreover, at the same time and as a matter of course, the foundations of chemical analysis as a genuine science were laid.

The failure of other workers.

Sufficient attention has not been given to the question, why it should have been left to Dalton to draw attention to the law of multiple proportion? It was not the want of interest in the subject of chemical composition. The workers on the subject, towards the end of the eighteenth and the beginning of the nineteenth century, were quite numerous. One may name Bergman, Wenzel, Klaproth, Lavoisier, Richter, Kirwan, Thomson, Bucholz, Chenevix,

[13] See the Faraday Lecture, *Trans. Chem. Soc.*, 1904.

Bostock, Clément, Désormes and Proust. Yet the failure of these chemists to discover the law of multiple proportion, despite their immense labours, was complete.

An incorrect explanation of the failure.

The reason usually offered for this failure is, that the data for the composition of substances were calculated in such a way as to hide the law.[14] Plainly the implication is, that the data calculated in a suitable way must reveal the law at once. This is mere guess-work, for as a matter of fact, data were frequently stated in precisely the way required. Proust, for instance, gives practically all his data for the oxides and sulphides of a metal, in terms of 100 parts of the metal.[15]

The true explanation.

The true explanation is twofold. In the first place, accurate chemical analysis is impossible without a check of some kind. That the analyst should have good intentions, even the best intentions, is not enough. In the absence of a guiding principle, chemists cannot tell when a substance is pure, or when an analysis is correct. As explained in the first paper of this series, it was this state of uncertainty which contributed at the beginning of the nineteenth century, more than anything else, to the spread of C. L. Berthollet's ideas regarding combination in indefinite proportions. Arrhenius has pointed out that every chemist *now* prepares his substances so that

[14] E. von Meyer, "Hist. of Chem.," Eng. trans., pp. 195-196, 1906, and Arrhenius, "Theories of Chem.," Eng. trans., p. 16, 1907.

[15] *Ann. de Chim.*, vol. 28, p. 214, 1798; *Jour. de Phys.*, vol. 54, p. 92, 1802; vol. 55, p. 330; vol. 59, p. 324, 326, 330, 352, 1804; vol. 62, p. 136, 138, 139, 1806: vol. 63, p. 431, 1806.

they agree with the laws of definite and multiple proportions.

In the second place Dalton was at an advantage over other workers, in having a theory to which he could refer facts. Something more is needed than important facts, one must have the eye to perceive their importance. Charles Darwin gives an illustration of this when he admits he once walked along a valley, full of the plainest indications of glacial action which he absolutely failed to notice. "On this tour I had a striking instance how easy it is to overlook phenomena, however conspicuous, before they have been observed by anyone. We spent many hours in Cwm Idwal, examining all the rocks with extreme care, as Sidgwick was anxious to find fossils in them; but neither of us saw a trace of the wonderful glacial phenomena all around us; we did not notice the plainly scored rocks, the perched boulders, the lateral and terminal moraines. Yet these phenomena are so conspicuous that, as I declared many years afterwards—a house burnt down by fire did not tell its story more plainly than did this valley."[16]

This is not a fanciful argument, but one that can be amply justified by facts. Chemists did not go on making analyses conscientiously without sometimes obtaining data in good agreement with the law of multiple proportion. But they quite failed to perceive the significance of the data. Dalton himself was able afterwards triumphantly to point out more than one such case, which had escaped the notice of the chemist concerned. He quotes Bostock's analyses of the acetate and superacetate of lead:—[17]

[16] "Life and Letters of Charles Darwin," 3 vols., 1887, vol. 1, p. 57.

[17] *Nicholson's Jour.*, vol. 11, p. 75, 1805; vol. 29, p. 150, 1811.

	Acetate.	Superacetate.
Lead	100	100
Acid	24	49

Again, he gives the instance of the oxides of carbon: "Carbonic oxide contains just half the oxygen that carbonic acid does, which indeed had been determined by Clément and Désormes . . . who, however, had not taken any notice of this remarkable result." [18]

[18] Roscoe and Harden, *op. cit.*, p. 117.

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XIX. The Development of the Atomic Theory:—(6) The Reception accorded to the Theory advocated by Dalton.

By Andrew Norman Meldrum, D.Sc.

(Communicated by Mr. R. L. Taylor, F.C.S., F.I.C.)

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"From the nature of the human mind, time is necessary for the full comprehension and perfection of great ideas." Thus the history of an idea necessarily includes the reception accorded to it on publication, and the steps by which it came to be of influence in the world.

Science, considered as an impersonal thing, advances by assimilating new and sound ideas. Yet this process of advancement, as the following paper shows, depends on the temperaments of individual men. The consideration of paramount importance in this respect is the fact that these men, according to their outlook on matters of theory, can be divided into two classes. There are (1) the men who are alive to the immense value of theory in science, and (2) the men who would confine science to a collection of facts and laws, as if it were "based entirely upon experiment or mathematical deductions from experiment."[1]

At any given time, the direction in which a particular branch of science advances is determined by a few persons only. Consequently, the men who are inimical

[1] P. G. Tait, "Recent Advances in Physical Science," p. 10.

to theory may exert a harmful effect on science, by despising and rejecting a theory of the utmost importance.

The usefulness to science of the atomic theory is so completely established now, that it must seem strange to us to observe the efforts Dalton had to make, in order to arouse attention to the importance of his ideas regarding atoms. For some nine years, (1801-1810), if not longer, he endeavoured to spread abroad his ideas, both by private communications and publicly, by his writings and by lectures in various parts of the country.

As will be seen, Dalton's speculations had to encounter dangers of two kinds. In the first place, not many people gave themselves much concern about the question of the continuity or discontinuity of matter. They were quite content to go on speaking of "atoms" and "molecules" in a vague, colloquial sense, and Dalton had to induce them, if possible, to use the words as terms of precision. This done, there was always the possibility that they would reject Dalton's idea of an atom as too hypothetical.

His physical atomic theory (described in the fourth paper of this series) was devised in the year 1801, from which time onwards he made many attempts to recommend it to the scientific world. But for years the only avowed adherent which it obtained was William Henry. The question at issue was a fundamental one, and Dalton's finding on it was ultimately triumphant. The theory expressed his conviction that the diffusion of gases is due to physical forces and not to chemical. But the prevailing tendency of the time was to regard diffusion as due to chemical affinity between the gases concerned, and the strength of that tendency was exhibited by the amount of opposition to Dalton's theory. Its opponents included

Thomas Thomson, John Murray, T. C. Hope, John Gough, Humphry Davy, and Claude Louis Berthollet.

Dalton's chemical theory was formed by the 6th September, 1803,[2] and he proceeded forthwith to extend and apply it, and make it known in every direction. His first efforts, naturally, were made at this Society, where, on the 7th October, he read a paper in which the theory was employed in order to explain the absorption of a gas by water. What he endeavoured to do was to establish a connection between the solubility of a gas and its atomic weight. This paper, as published in 1805, comes to an end with a table of atomic weights, of various simple and compound substances, remarkable as the earliest of the kind ever printed. There is no reason to doubt that the paper contained a table of atomic weights when it was read, but Dalton certainly extended the table before going to press.

Dalton was eager both to have his ideas put into circulation and to have a resumé of them put on record. In London, in the winter of 1803-1804, he gave a course of lectures at the Royal Institution, in which he included a brief outline of the theory. He left this for publication in the Journals of the Institution, but, as he ironically remarked afterwards, "he was not informed whether that was done."[3] Humphry Davy was at the Institution at the time, but Dalton did not succeed in arousing in him

[2] A paper of his, read before this Society on November 12th, 1802, contains a reference to the chemical theory. This is the paper "on the proportion of the several gases, or elastic fluids, constituting the atmosphere." But it was not published till 1805, and Roscoe and Harden think it was re-written in the meantime, for it includes results, on the combination of nitric oxide and oxygen, which Dalton did not obtain till 4th August, 1803. (Roscoe and Harden, "New View of the Origin of Dalton's Atomic Theory," p. 35). I cannot myself doubt that this conclusion is the correct one.

[3] "New System of Chemical Philosophy," 1808, Preface.

any interest in the theory, much less any enthusiasm for it. In a course of lectures which he gave in Manchester in 1805, he included an account of the theory.[4] But it was not taken up there for years, not even by William Henry. There is not the slightest sign that Dalton would not have welcomed workers on the subject. But the atoms were counted an airy or recondite speculation. Dalton's atomic weight data caused no thrill of excitement, aroused no eager curiosity, no consuming wish to join in his work.

In North Britain Dalton had a different reception. Early in the year 1807 he gave a course of lectures, twice in Edinburgh and once in Glasgow. In Edinburgh he says "a class of eighty appeared for me in a few days." At the conclusion "several of the gentlemen who had attended the course represented to me that many had been disappointed in not having been informed in time of my intention to deliver a course, and that a number of those who had attended a first course would be disposed to attend a second."[5] This reception afforded Dalton precisely the encouragement of which he stood in need. "On these occasions," he said, "he was honoured with the attention of gentlemen, universally acknowledged to be of the first respectability for their scientific attainments: most of them were pleased to express their desire to see the publication of the doctrine in its present form, as soon as convenient. Upon the author's return to Manchester he began to prepare for the press."[6]

[4] Two unpublished papers, read before the Manchester Society in 1804, probably included accounts of the theory. The titles are respectively "A Review and Illustration of some Principles in Mr. Dalton's course of lectures on Natural Philosophy at the Royal Institution in January, 1804," and, "On the Elements of Chemical Philosophy."

[5] Angus Smith, "Memoir of Dalton," p. 58.

[6] "New System of Chemical Philosophy," 1808, Preface.

In the "New System of Chemical Philosophy" both the Preface and the Dedication show that Dalton was immensely grateful for the attention his speculations received in Glasgow and Edinburgh. The dedication runs:—"To the Professors of the Universities and other residents of Edinburgh and Glasgow who gave their attention and encouragement to the Lectures on Heat and Chemical Elements, delivered in those cities in 1807: and to the members of the Literary and Philosophical Society of Manchester, who have uniformly promoted his researches."

An account of the theory, often referred to in this series of papers, had already appeared. Thomas Thomson had been so much interested and impressed by the doctrine as Dalton explained it to him in 1804, that he became the first convert to it. He showed as much zeal in the cause as its author. With permission he gave a short sketch of it in the next edition of his "System of Chemistry." This was the third edition, published in 1807, of the most successful treatise of the day on chemistry, and it had more influence, directly, in spreading a knowledge of the doctrine than Dalton's own efforts. It made Dalton's theory known to William Hyde Wollaston in London, to Claude Louis Berthollet in France, and to Amadeo Avogadro in Italy.

Thomson found another opportunity of expounding the theory in his memoir "On oxalic acid," which appeared in the *Philosophical Transactions* of the Royal Society of London in 1808. The very next paper in the *Transactions* is one by Wollaston—on the carbonates and oxalates of potassium—and he, as well as Thomson, advanced his work as exemplifying and justifying Dalton's theory. By these various means, Dalton's and Thomson's books,

and Thomson's and Wollaston's memoirs, it became known in Britain and France, in Italy and Sweden.

Not only in these ways, but by personal exertions, Thomson and Wollaston sought to advance the theory. In his "History of Chemistry," Thomson gives a narrative of the efforts that had to be made to induce Humphry Davy to take it seriously. Long as the narrative is, it is quoted here almost in full, for it illustrates the fact that in science the spread of new ideas depends as much on personal efforts, springing from genuine conviction, as on printed papers. It would seem that Thomson and Wollaston failed themselves to persuade Davy. Wollaston, however, converted Davies Gilbert, and he, in his turn, succeeded in converting Davy.

"Some of our most eminent chemists," says Thomson, "were very hostile to the atomic theory. The most conspicuous of these was Sir Humphry Davy. In the autumn of 1807 I had a long conversation with him at the Royal Institution, but could not convince him that there was any truth in the hypothesis. A few days after I dined with him at the Royal Society Club, at the Crown and Anchor in the Strand. Dr. Wollaston was present at the dinner. After dinner every member of the club left the tavern, except Dr. Wollaston, Mr. Davy, and myself, who staid behind and had tea. We sat about an hour and a half together, and our whole conversation was about the atomic theory. Dr. Wollaston was a convert as well as myself; and we tried to convince Davy of the inaccuracy of his opinions, but, so far from being convinced, he went away, if possible, more prejudiced against it than ever. Soon after, Davy met Mr. Davis [*sic*] Gilbert, the late distinguished president of the Royal Society, and he amused himself with a caricature description of the atomic theory, which he exhibited in so ridiculous a light, that Mr. Gilbert

was astonished how any man of sense could be taken in with such a tissue of absurdities. Mr. Gilbert called on Dr. Wollaston (probably to discover what could have induced a man of Dr. Wollaston's sagacity and caution to adopt such opinions), and was not sparing in laying the absurdities of the theory, such as they had been represented to him by Davy, in the broadest point of view.

"Dr. Wollaston begged Mr. Gilbert to sit down, and listen to a few facts which he would state to him. He then went over all the principal facts at that time known respecting the salts; mentioned the alkaline carbonates and bicarbonates, the oxalate, binoxalate, and quadroxalate of potash, carbonic oxide and carbonic acid, olefiant gas and carburetted hydrogen; and doubtless many other similar compounds, in which the proportion of one of the constituents increases in a regular ratio. Mr. Gilbert went away a convert to the truth of the atomic theory; and he had the merit of convincing Davy that his former opinions on the subject were wrong."[7]

Thomson goes on to say that Davy "ever after was a strenuous supporter" of the atomic theory. This puts his support of the theory far beyond its true value. Davy was never enthusiastic about the doctrine of atoms as such, and he much preferred the term "proportion" to "atom." The following passage, published in 1811, probably represents his mature opinion on the subject:— "it is not, I conceive, on any speculations upon the ultimate particles of matter, that the true theory of ultimate proportions must ultimately rest."[8]

Dalton himself was far from satisfied with the reception accorded to his theory. Hope, of Edinburgh,

[7] Thomson, "History of Chemistry," vol. 2, p. 293.

[8] *Phil. Trans.*, 1811, Bakerian Lecture, or Davy's Works, vol. 5, p. 326.

could not bring himself to accept it.[9] It was criticised adversely by Dr. Bostock in *Nicholson's Journal*, and Dalton, in reply, quoted in support of it analyses by Dr. Bostock. He then remarks :—"A number of such analyses as these would compel Dr. Bostock and others of your chemical readers to examine the theory of chemical combinations which I have offered to them with more attention, than I fear they do. The present state of chemical science imperiously demands it,"[10]

In France, also, the theory was coldly received. Berthollet naturally opposed it, for in its general tendency it condemned his attempt to obliterate the distinction between physical and chemical forces, and, in particular, it was contradictory of his doctrine of chemical combination in indefinite proportions (see the first paper of this series). He considered Dalton's theory too hypothetical, and his opposition had great influence. Gay-Lussac, who had been his pupil, was unable to "rid himself of preconceptions due to early training." In his famous memoir, on the proportions by volume in which gases combine, he remained an adherent of Berthollet.

Gay-Lussac was always timid in matters of theory. Such was his temperament. On one occasion he laid it down that "in natural science, and, above all, in chemistry, generalisation should come after, and not before, a minute knowledge of each fact."[11] Such a man was not very likely to subscribe to a doctrine like Dalton's, which *promised* to transform the whole province of chemistry. Gay-Lussac admitted the *facts* adduced by Dalton and Thomson and Wollaston, and that was all.

Gay-Lussac conceded to Dalton as much as he must, and nothing more. From his own results it seems obvious

[9] Roscoe and Harden, *op. cit.* p. 153.
[10] *Nicholson's Journal*, vol 29, p. 150, 1811.
[11] *Ann. Chim. Phys.*, vol. 11, p, 297, 1819.

now that there must be very simple ratios between the volumes occupied by different atoms in the gaseous state. Many writers[12] have assumed that Gay-Lussac, in his memoir, defined the relation between his law and the atomic theory, but, as a matter of fact, he ignored it. He did not recognise the theory, and the subject was neglected and came to nothing in France for years. At length, in 1814, Ampère published a memoir,[13] of which the fundamental idea is that the molecules of different gases under the same conditions have the same size, so that equal volumes of different gases contain the same number of molecules. In this memoir, the first outcome of the modern atomic theory in France, Dalton is not mentioned.

In Italy Amadeo Avogadro had forestalled Ampère by three years.[14] Under the stimulus of Dalton's speculations, of which he had learnt through Thomson's "System of Chemistry,"[15] he composed the memoir in which he advanced and maintained his famous hypothesis, that under the same conditions the molecules of different gases occupy the same volume. This hypothesis, involving as it did a distinct departure from Dalton's ideas, became the fundamental dogma of molecular science only after the lapse of fifty years.

In Sweden J. J. Berzelius had been occupied for some time in determining the composition of metallic salts, when Wollaston's memoir reached him.[16] Forthwith he set

[12] See, for instance, Clerk Maxwell, "Theory of Heat," 10th ed., p. 326.

[13] *Ann. Chim.*, vol. 90, pp. 43-86, 1814.

[14] *Jour. Phys.*, vol. 73, pp. 58-76, 1811.

[15] "In what follows, I shall make use of the exposition of Dalton's ideas which Thomson has given us in his 'System of Chemistry,'" *loc. cit.*, p. 62.

[16] *Phil. Mag.*, vol. 41, p. 3, 1813.

himself the task of testing the validity of Dalton's theory on the grand scale. As he said, "this way of regarding chemical compounds at once throws such a clear light on the doctrine of affinity, that if the hypothesis of Dalton could be proved, it should count as the greatest step that chemistry had made towards its perfection as a science."[17]

As Lord Morley has pointed out, the people who launch great ideas on the world are seldom the people who apply them. Dalton's and Thomson's efforts to make the atomic theory widely known were really far more valuable than the concrete results they obtained by the use of it. Dalton himself was involved by the theory in a "labyrinth of chemical investigation," where he wandered for many years and wasted his energies. It was Berzelius, and no other, who applied it, made it the foundation of accurate chemical analysis, and proved it to be an organon of incomparable power for the advancement of chemistry.

[17] *Loc. cit.*

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XXII. The Development of the Atomic Theory: (7) The rival claims of William Higgins and John Dalton.

By Andrew Norman Meldrum, D.Sc.

(Communicated by Mr. R. L. Taylor, F.C.S., F.I.C.)

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The rival claims of William Higgins and John Dalton to the atomic theory were much discussed early in the nineteenth century. The result of the discussion was, on the whole, favourable to Higgins. But from a variety of reasons, this result has been forgotten, and Dalton's claims are supposed at the present time to be beyond dispute. The author, in reviving the subject, hopes to present the facts, and to offer considerations, so as to enable anyone interested to come to a simple and fair conclusion upon it.

With the above purpose in view, it is necessary to consider the question, What is the essence of Dalton's atomic theory? This question, one of much interest, has proved in the experience of writers on the subject, one also of much difficulty. An answer to it, which cannot be set aside, has recently been given by Larmor. In his Wilde Lecture—"On the Physical Aspects of the Atomic Theory"—he has expressed the Daltonian principle in the words "a definite molecule for each substance." He explains this more fully as follows:—"Perhaps the new feature developed by Dalton is at bottom describable as the principle of

the essential homogeneity of each pure substance, that it is composed of molecules of only one type, absolutely alike. Once it is postulated that only one kind of aggregation into molecules occurs, *e.g.*, that in water there is only one way in which the hydrogen attaches itself to the oxygen, the laws of definite and multiple proportions are self-evident."[1]

Undoubtedly this principle, "a definite molecule for each substance," is common to the various systems of chemistry of the nineteenth century. Yet the principle was not necessarily advanced first by Dalton. I have already shown (in the third paper of this series) that William Higgins expounded a definite chemical atomic theory in a book which he published in the year 1789. Further, the words, a "definite molecule for each substance," give, as will presently appear, an unexceptionable statement of the theory contained in Higgins' book.

The two theories, Higgins' and Dalton's, led their authors, in a remarkable degree, to the same results. This is proved by the following table, the formulæ in which reveal at once the ideas which Higgins and Dalton had regarding the molecules of the substances in question:

	Higgins (1789).	Dalton (1803).
Water	HO	HO
Ammonia	—	HN
Oxides of sulphur ...	SO and SO_2	SO and SO_2
,, carbon ...	—	CO and CO_2
,, nitrogen...	NO, NO_2, NO_3, NO_4 and NO_5	N_2O, NO and NO_2

The great similarity between these results is to be explained in only one way. The two theories have in common, as a guiding principle, the rule that atoms of

[1] *Manchester Memoirs*, 1908, **52**, No. 10, p. 9.

different kinds combine in the proportion 1 : 1 rather than in any other. It was this rule, and no other, which led each chemist to precisely the same conclusions regarding water, and the oxides of sulphur, respectively.

How the rule was arrived at is a matter of the historical origin of the theories. As I have already shown, they arose from the same central capital idea: Newton's postulate of "particles mutually repulsive" was the starting point in each case. The thoughts of each chemist ran in the same groove. Similar particles repel one another, consequently particles of different kinds tend to unite in pairs.

Bryan Higgins was the first to reach this stage of thought, and he would not depart from it in any way. He supposed that the combination of one atom of alkali and two atoms of acid (or two of alkali and one of acid) must be prevented by the mutual repulsion of the two similar atoms, so that combination could not proceed further than 1 : 1.

Better acquainted than he with the facts of chemical combination, William Higgins imagined the combination of atoms in multiple proportion. But he laid it down that the combination in the proportion 1 : 1 was the most stable, thus adhering to the original idea of mutually repulsive particles.

The train of thought which Dalton followed had features of its own. His physical atomic theory was plainly an extension of Newton's, and was called for by the discovery of the existence of different gases, of their property of diffusing into one another, and of the properties of the resulting mixture. As I have shown in the fifth paper of this series, he held the physical theory for two years before he formed the chemical one. He was able

to devise the latter in the space of a month, simply because he had the former to work upon.

The close resemblance between the two theories, both in principle and results, puts it beyond doubt that Dalton was forestalled by William Higgins. Humphry Davy, in his Bakerian Lecture of the year 1810, was the first to draw attention to Higgins' claims. The terms in which he did so are remarkably decided, and such as to throw him into almost too pronounced antagonism to Dalton. "In my last communication to the [Royal] Society, I have quoted Mr. Dalton as the original author of the hypothesis that water consists of 1 particle of oxygen and 1 of hydrogen, but I have since found that this opinion is advanced in a work published in 1789—'A Comparative View of the Phlogistic and Antiphlogistic Theories,' by William Higgins. In this elaborate and ingenious performance, Mr. Higgins has developed many happy sketches of the manner in which (on the corpuscular hypothesis) the particles or molecules of bodies may be conceived to combine; and some of his views, though formed at this early period of investigation, appear to me to be more defensible, assuming his data, than any which have been since advanced."[2]

The only public notice which Dalton himself took of Davy's words was to publish a paper in which he was careful not to name Higgins. The date of Davy's lecture was 15th November, and of Dalton's paper 19th December. He contended that the use of the word *particle*, as opposed to *atom*, was a matter of great consequence—a contention which was quite unworthy of him.[3]

[2] Bakerian Lecture, 15th Nov., 1810, *Phil. Trans.*, 1811, p. 15; Davy's Works, vol. 5, p. 326.

[3] *Nicholson's Journ.*, vol. 28, p. 81, 1811.

Though Davy saw fit afterwards to qualify this declaration, he could never undo the effect it produced. No one was better able than he to make Higgins known at once, for he was famous throughout Europe. His papers were read by all scientific men: thus Berzelius and Arago each mention that their attention was drawn to Higgins by Davy. The consequence in this country was a long and desultory controversy regarding the respective claims to the atomic theory of William Higgins and John Dalton.

In the course of the controversy the suggestion was made that Dalton had been guilty of plagiarism at the expense of Higgins. The charge was made far too lightly.[4] Dalton was not a great reader, and it was very unlikely he would look twice at a book which dealt, on the face of it, expressly with the phlogiston controversy. But it was necessary that a statement on the subject should be made, and the statement was forthcoming. Thomas Thomson declared that Dalton had no knowledge of Higgins' book previous to the year 1810, and this declaration was made repeatedly afterwards by Dalton's personal friends.[5]

It is easy to account for the resemblance between the two theories. They had a common origin in Newton's ideas, and there is no need for any other explanation.

[4] Du Bois Reymond and Helmholtz each hit upon the same illustration of the time taken by a nervous impulse. "A whale probably feels a wound near its tail in about a second, and requires another second to send back orders to the tail to defend itself." "Hermann von Helmholtz," by von Kœnigsberger, Eng. trans., 1906, p. 72.

[5] Thomson, *Annals of Phil.*, 4, 54, 1814; William Henry, "Elements of Experimental Chemistry," 11th ed., 1829, 1, 45; W. C. Henry, "Memoirs of Dalton," pp. 78, 175, 217.

Thomas Thomson was Dalton's champion during the controversy, and he stoutly resisted Higgins' claims. The position he adopted is a specially interesting one. He declared that although Higgins' book had been widely read, no one had perceived the atomic theory in it. He therefore denied that the theory was there. This is not an answer, however, but an argument, and one that Thomson could hardly have used if he had kept in mind the reception Dalton's theory met with when it was launched upon the world. (See the sixth paper of this series.)

Humphry Davy, for instance, ignored it for long, and disparaged it when it was forced upon his notice. One can hardly wonder, then, that Higgins' speculations should have been disregarded, for they appeared many years before, under cover of a contribution to the phlogiston controversy.

Thomson, however, offered the testimony that he himself had failed to perceive the theory in Higgins' book. "I have certainly affirmed that what I consider as the atomic theory was not established in Mr. Higgins' book... I have had that book in my possession since the year 1798, and had perused it carefully; yet I did not find anything in it which suggested to me the atomic theory. That a small hint would have been sufficient I think pretty clear from this, that I was forcibly struck with Mr. Dalton's statement in 1804, though it did not fill half an octavo page."[6]

This is hardly enough to establish Thomson's case. It amounts to the plea that he was not making a mistake in the year 1814, simply because he could not have made it in the year 1798. Charles Darwin was a humbler

[6] *Annals of Phil.*, 3, 331, 1814.

man. As mentioned in the fifth paper of this series, he confessed that he and Sidgwick once passed along a valley without observing signs of glacial action, which were, none the less, present everywhere. They failed to perceive these signs because they were directing their attention to something else. In the same way the atomic theory may be in Higgins' book even though Thomson failed to perceive it.

As a result of the controversy, it appeared that most chemists were unable to deny Higgins' claims. William Hyde Wollaston observed that Mr. Higgins "in his conception of union by ultimate particles clearly preceded Mr. Dalton in his atomic views of chemical combination."[7] Thomas Graham, again, in his "Chemical Catechism," puts the question, "Who first made use of the atomic hypothesis in chemical reasonings?" The answer is:—"A Mr. Higgins, of Dublin—in a book of his published in the year 1789."[8]

Again, it is true that William Higgins has been almost forgotten. After his death, in 1825, he gradually passed out of notice and recollection. The claims of Dalton, on the other hand, have been advocated by a succession of Manchester chemists, including W. C. Henry, R. Angus Smith, and Roscoe and Schorlemmer. These writers have thought to advance their cause by disparaging Higgins, but, as I have shown in the third paper of this series, their criticisms are unfair, and must be set aside.

As I have already said, inasmuch as the "Daltonian principle, a definite molecule for each substance," is the principle also of Higgins' theory of the year 1789, there is no avoiding the conclusion that Higgins forestalled

[7] *Phil. Trans.*, 1814, p. 5.

[8] "Chemical Catechism," 1829, p. 35.

Dalton. This is no small merit, for the said principle is the central idea of all the atomic weight systems of the nineteenth century.

It is, however, a great mistake to suppose that this conclusion exhausts the subject of the merits of the two chemists. Humphry Davy, years after his declaration on behalf of William Higgins, saw that there was something more to be said. He recognised the claims of Bryan Higgins :—" It is difficult not to allow the merits of prior conception, as well as of very ingenious illustration, to the elder writer." [9] He said, further, " Let the merit of discovery be bestowed where it is due, and Mr. Dalton will be still pre-eminent in the history of the theory of definite proportions." [10]

It is true on the one hand, that William Higgins was much indebted to Bryan Higgins, and on the other hand, that he left the atomic theory capable of infinite development by other chemists. It can be urged against him that he did not work out the practical consequences of his ideas. Why did he not make use of his ideas as a guide in experimental work? It might be supposed that he did not attach much importance to them, or he would surely have made strenuous exertions to establish them experimentally, and to make them known. But, as a matter of fact, there is nothing in his writings to show that he had anything but a high opinion of his theory. In the year 1799, seizing the opportunity of the publication of a book of his on bleaching, to draw attention to his system of chemistry, he declared that he had "connected the whole, and reduced it to a system, and made use of demonstrations which, in his opinion, are not to be invalidated or contra-

[9] Davy's Works, 7, 93.

[10] *Op. cit.*, p. 96.

dicted, until the order of natural things assume a different aspect."[11]

The strain of thought here is exalted enough to raise a smile, and, moreover, to prove the high value that Higgins set on his speculations. Elsewhere he stated that he taught the atomic theory in his lectures at the Royal Dublin Society. "What is called the atomic theory formed a part of my annual course of lectures."[12]

Higgins thus exemplifies "faith without works." He had splendid ideas which he did not work out. More than one writer commented on this. Wollaston remarked that "he appears not to have taken much pains to ascertain the actual prevalence of that law of multiple proportions by which the atomic theory is best supported."[13] Davy, in his obituary notice of Higgins, passed a very severe judgment upon him: ". . . . it is impossible not to regret that he did not establish principles which belong to the highest department of chemistry, and that he suffered so fertile and promising a field of science to be entirely cultivated by others; for though possessed of great means of improving chemistry, he did little or nothing during the last thirty years of his life."[14]

William Higgins (saving his indebtedness to Bryan Higgins) stands in much the same relation to the chemical atomic theory as J. A. R. Newlands to the periodic system of the elements. Newlands foreshadowed the periodic system in its most important features. Although his ideas were scouted by the officials of the Chemical Society of London, he adhered to them, and was enabled to publish

[11] "An Essay on the Theory of Bleaching," 1799, p. xx.

[12] *Phil. Mag.*, 1819, 53, 405.

[13] *Phil. Trans.*, 1814, p. 5.

[14] Davy's Works, 7, 75.

them by the open-mindedness of the Editor of the *Chemical News.* In Higgins' case, as in Newland's, we find an idea of extraordinary potency advanced by a man, who for some reason or other, leaves the idea almost in the germ and capable of infinite development by the efforts of others. Moreover, it was not through Higgins and Newlands that these ideas came to have an influence on the progress of science.

Granting the utmost that can be said on behalf of Higgins, one must admit that Dalton made a great contribution to the development of the atomic theory. Much the superior of Higgins in energy of character and mind, he made himself a prime factor in the development of the theory by the persistency of his efforts to extend and apply it in all directions, and to bring it into currency amongst men of science. He applied it first to physical and then to chemical phenomena. In opposition to Berthollet's erroneous teaching regarding mixed gases and the composition of chemical substances, he offered sound ideas based on the theory. Again, he perceived, far more clearly than Higgins, the practical consequences of the combination of atoms. He never delayed putting his ideas to the test of experiment. The test was often hastily and crudely made, so urgently did he feel the necessity of making it. No one can say that the chemical atomic theory was accurately verified by Dalton, and no one can deny that his table of atomic weights brought the theory into touch with facts, and showed to all with eyes to see, exactly what the theory meant. It has already been shown, in the sixth paper of the series, that Dalton converted Thomas Thomson to the theory, that Thomson influenced William Hyde Wollaston, and Amadeo Avogadro, and that Wollaston influenced J. J. Berzelius.

In preparing this series of papers, I made constant use of the "Royal Society Catalogue of Scientific Papers," and the "Select Bibliography of Chemistry," published by the Smithsonian Institution.[15] On bringing the series to an end, I desire to acknowledge my indebtedness to the libraries of the following institutions: The Victoria University of Manchester, Aberdeen University, The Manchester Literary and Philosophical Society, and The Glasgow and West of Scotland Technical College. At the same time I would tender my most grateful thanks to the respective librarians, Mr. Charles Leigh, Mr. P. J. Anderson, Mr. A. P. Hunt, and Mr. Peter Bennett, for the cordial way in which they facilitated my work.

[15] Smithsonian Miscellaneous Collections, Nos. 850, 1170, and 1440.